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INTRODUCTION TO THE STUDY
OF
ORGANIC CHEMISTRY.

THE CHEMISTRY
OF
CARBON AND ITS COMPOUNDS.

AGRICULTURAL
EXPERIMENT STATION.

DEC 1 1883
BY UNIVERSITY OF ILLINOIS

HENRY E. ARMSTRONG, PH.D., F.R.S., SEC.C.S.

Professor of Chemistry in the London Institution:

Late Assistant Examiner in Chemistry in the University of London.

FIFTH EDITION.

LONDON :
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# PREFACE

TO

## THE SECOND EDITION.

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THE extraordinary progress of Organic Chemistry during the last few years and the experience gained since the publication of the first edition of this book would lead me to recast much of it, if not to remodel the entire work ; but for various reasons, and especially on account of the difficulty of dealing with stereotype plates, I am unable to do this at present. I have, however, endeavoured to correct errors which I had made, or which recent investigations have disclosed ; and besides doing this I have re-written a few sections, such as those on the terpenes, on the carbohydrates, and on the action of sodium on ethylic acetate, in order that they may more nearly represent the present state of knowledge. I have also entered at some length into a description of Kekulé's benzene theory, which appears now to be established on an irrefragable experimental basis. I trust that these alterations and additions will have so increased the value of the work that it may ere long be my privilege to endeavour to improve it further.

*1180, C. D.*

The first part deals with the methods employed in ascertaining the composition of Carbon Compounds ; the representation of carbon compounds by empirical formulæ, and by formulæ which not only express their composition, but also to a certain extent picture their nature, is then briefly discussed. After a short description of the action of various reagents on carbon compounds, the compounds of carbon with oxygen, with sulphur, and with nitrogen, are briefly considered. The great family of hydrocarbons are next described ; and the remaining families of carbon compounds are then considered in the order of their relation to the hydrocarbons, which are regarded as forming the parent series.

A very large number of substances have necessarily remained unnoticed ; in fact, with few exceptions, only those compounds have been described of which the relations to other well-understood bodies have been satisfactorily established, the object of this work being to assist the systematic study of carbon compounds, and to draw attention to the intimate relations which exist amongst them, rather than to enumerate and describe individual compounds.



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# ORGANIC CHEMISTRY.

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## CHAPTER I.

### INTRODUCTION.

CHEMISTRY being defined as the study of the nature and properties of the various *elements*; of the laws according to which these elements enter into combination with each other; and of the nature and properties of the compounds formed by their union; organic chemistry may be generally defined as the chemistry of *carbon* and its compounds, since carbon is the one *essential* element in all organic compounds.

The separation of chemical science into the two branches of inorganic and organic chemistry is in reality arbitrary, but it is convenient, simply on account of the enormous number, and special importance, of the compounds included in the latter division; not that they are in any way subject to different laws from those which govern inorganic compounds.

By the older definition, only such bodies as were formed within the animal or plant were included in the category of organic compounds. It was generally held that the interposition of the so-called *vital force* was absolutely essential to their formation, and their artificial production was therefore regarded as impossible. This idea, however, was disproved

by the synthesis<sup>1</sup> of *urea*, a crystalline substance secreted in the urine of man and mammiferous animals, effected by Woehler in the year 1828, and since that time many other organic bodies which occur naturally have been artificially produced.

The most important organic substances met with in nature are those in which carbon is associated in various multiple proportions with the elements hydrogen and oxygen ; next in importance are those containing nitrogen in addition to these ; sulphur and phosphorus also are present in some few. A very large number have been obtained artificially, containing either chlorine or bromine, iodine, silicon, or one or other of the metals ; in fact, there is little doubt that any of the known elements may enter into the composition of carbon compounds.

#### DETERMINATION OF THE COMPOSITION OF CARBON COMPOUNDS.

1. *Estimation of Carbon and Hydrogen.*—All organic substances, when burnt under favourable conditions with a sufficiency of oxygen, yield the whole of their carbon in the form of carbonic anhydride ( $\text{CO}_2$ ), and their hydrogen in the form of water. In order therefore to determine qualitatively the presence of carbon and hydrogen, the substance is heated to redness either in oxygen gas, or mixed with an easily reducible metallic oxide, such as cupric oxide ( $\text{CuO}$ ), and the gaseous products are passed first through a cold dry tube, and then into lime or baryta water. Provided that all the materials employed, and all parts of the apparatus, were in the first instance perfectly dry, the deposition of water in the cold tube, and the formation of a white precipitate (calcic or baric carbonate) in the lime or baryta water, would afford conclusive proof that the substance examined contained both carbon and hydrogen.

<sup>1</sup> Synthesis : putting together.

The quantitative estimation of these two elements is in principle the same, and simply consists in determining the *amounts* of carbonic anhydride and water yielded by a known weight of substance. In the following an outline of the method usually employed is given :—

The combustion, as the operation is termed, is performed in a tube of hard Bohemian glass, drawn out at one end to a fine point and closed (fig. 1). This tube must be perfectly dry. A length of about five inches at the closed end is filled with granulated, freshly-ignited cupric oxide, and if the substance to be analysed is solid,<sup>1</sup> a weighed quantity of it (·3–·5 grm.), in as finely-divided a state as possible, is then introduced, rinsed down the sides of the tube by fresh cupric oxide, and intimately mixed therewith by means of a long polished brass wire terminating in a spiral (fig. 2). The tube is afterwards filled to within about two inches of the open end with cupric oxide, and the tared apparatus for collecting the water is attached by means of a well-fitting, dry cork ; it is then placed in the furnace, and the tared bulbs in which the carbonic anhydride is to be absorbed are attached to the drying tube by a short length of caoutchouc tubing. The disposition of the entire apparatus will be evident from fig. 3.

The drying tube A contains porous pieces of calcic chloride, which readily absorbs water, but does not retain carbonic anhydride ; or pieces of pumice soaked in concentrated sulphuric acid ; the latter being preferable owing to its superior desiccating powers. The bulb apparatus B, in which the carbonic anhydride is retained, is filled with a solution of potassic hydrate, prepared by dissolving one part of the solid in two parts of water.

The tightness of the various junctions having been ascertained, the fore part of the tube containing only cupric oxide is heated to redness ; when red hot, the mixture of substance

<sup>1</sup> If the substance is liquid it must be sealed up in a small weighed glass bulb with a narrow stem drawn out to a fine point ; this is again weighed, the fine point is broken off, and the bulb is dropped into the tube. Oily or fatty bodies are placed in a porcelain or platinum boat, which is pushed down the tube.



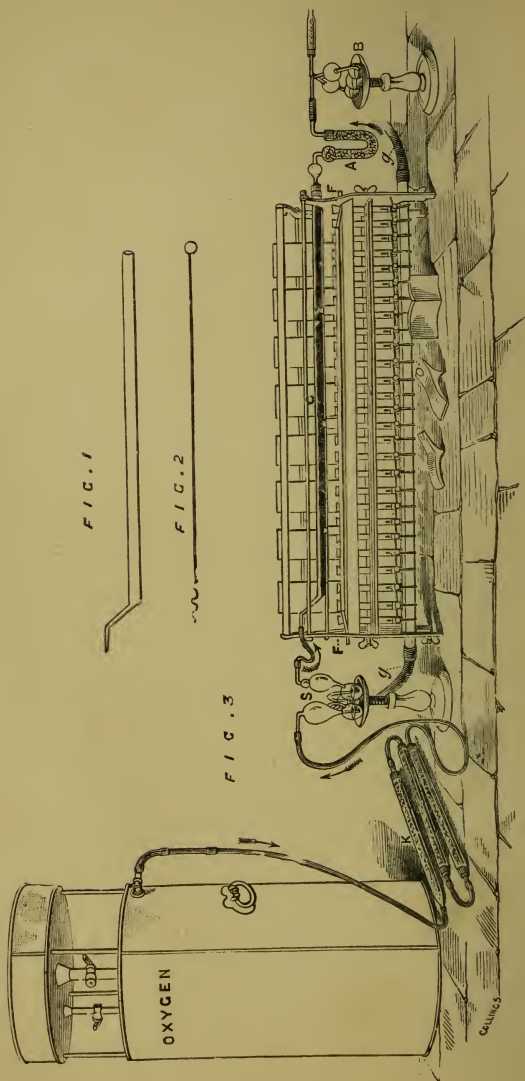


FIG. 3.—F F, Gas combustion furnace. g g, Tubing in connection with gas supply. c, Combustion tube. κ, Tubes containing pieces of potassic hydrate. S, Bulbs containing concentrated sulphuric acid. A, Drying tube. B, Potash bulbs.



and cupric oxide is carefully heated, commencing at the end of the tube most distant from the absorption apparatus. The vapours of the substance then become entirely burnt to carbonic anhydride and water, in their passage over the red-hot cupric oxide: the water collects in the drying tube, and the carbonic anhydride is retained in the potash bulbs. The heat must be so regulated that a slow, uniform stream of gas bubbles passes into the bulbs. So soon as the tube is heated to redness from end to end, and gas ceases to be evolved, the fine point of the combustion tube is broken off, and, by means of an aspirator attached to the potash bulbs, a slow stream of air is drawn through the apparatus in order to carry over the carbonic anhydride and aqueous vapour remaining in the tube into the absorption apparatus.

A better plan, however, is to connect the point of the tube with a gasholder filled with oxygen, and, after breaking off the point, to force a current of that gas through the tube. The oxygen must be previously passed through several tubes filled with pieces of solid potassic hydrate, and through concentrated sulphuric acid, in order to free it from all traces of carbonic anhydride and moisture. In this way, not only is the carbonic anhydride remaining in the tube swept over into the potash bulbs, but any portions of carbon which may have escaped combustion by the cupric oxide—and when difficultly combustible substances are burnt, this often occurs—are also converted into carbonic anhydride.

The potash bulbs and drying tube are then detached, allowed to cool down to the temperature of the balance case, and weighed. The increase of weight represents the amounts of carbonic anhydride and water yielded by the combustion of the weight of substance employed. From these data it is easy to calculate the percentage composition of the body analysed.

Since every 44 parts of carbonic anhydride contain 12 parts of carbon, or every 11 parts 3, the amount of carbon in the weight of substance burnt is obtained by multiplying the weight of carbonic anhydride formed by 3 and dividing the product by 11. Similarly, by dividing the weight of water by 9, we obtain the weight of hydrogen.

$$C = CO_2 \frac{3}{11}. \quad H_2 = \frac{H_2O}{9}$$

By simple rule of three—multiplying the amounts of carbon and hydrogen obtained by 100, and dividing the products by the weight of substance taken—we then ascertain the number of parts of carbon and hydrogen of which every 100 parts of the substance consist.

For example, the following numbers were obtained by combustion of turpentine-oil :

·2500 grm. gave ·8085 grm.  $\text{CO}_2$ , and ·2655 grm.  $\text{OH}_2$ .

Now ·8085 grm.  $\text{CO}_2$  = ·2205 grm. C ; and ·2655 grm.  $\text{OH}_2$  = ·0295 grm. H ; hence every 100 parts of turpentine-oil consist of :

|          |              |
|----------|--------------|
| Carbon   | 88·20        |
| Hydrogen | 11·80        |
|          | <hr/> 100·00 |

When substances containing nitrogen are burnt with cupric oxide, the greater part of the nitrogen is evolved as such, but a portion is always oxidised, and if nitric oxide is formed, it becomes converted into nitric peroxide on meeting with air in the potash bulbs, which is absorbed by the potassic hydrate, thus rendering the carbon determination inexact. This source of error, however, is readily eliminated by placing a roll of metallic copper in the fore part of the tube in front of the cupric oxide. If kept at a bright red heat during the combustion, this decomposes any oxide of nitrogen, itself absorbing the oxygen and setting free the nitrogen.

It is often necessary to substitute plumbic chromate for cupric oxide : compounds containing chlorine or bromine yield, when burnt with cupric oxide, volatile cupric chloride, or bromide, which condense in the drying tube ; sulphur compounds yield sulphurous anhydride, which is absorbed in the potash bulbs, and salts of the alkali metals yield a residue of metallic carbonate, which is not decomposed in contact with cupric oxide, so that too little carbonic anhydride is obtained.

If such substances are burnt with plumbic chromate, however, non-volatile plumbic chloride, bromide, and sulphate are formed, and the alkali salts are entirely decom-

posed. The use of plumbic chromate is also advisable in the case of difficultly combustible substances.

Determinations thus made are of course never absolutely correct—there is always a certain amount of experimental error. The carbon determination is usually from one to two-tenths per cent. too low, owing chiefly to incomplete combustion; the hydrogen about the same amount too high, in consequence of the imperfect removal of adherent moisture from the combustion tube and other materials employed.

*Determination of Nitrogen.*—The majority of nitrogenous organic substances, when strongly heated with potassic, or sodic hydrate, give off the whole or part of the nitrogen which they contain in the form of ammonia, but the following is the only test which permits the detection of nitrogen in all cases :

The suspected substance is heated with a small piece of potassium or sodium, when violent reaction usually takes place; the mass is dissolved in water, the solution filtered, a few drops of ferrous sulphate and ferric chloride solutions are added, and then an excess of hydrochloric acid. If a blue precipitate (Prussian blue) remain, or is deposited from the greenish solution on standing, nitrogen is present. (For explanation of the reactions which occur, see p. 62.)

Nitrogen may be readily estimated in compounds from which the whole of the nitrogen is evolved as ammonia on heating with caustic alkali, by igniting an intimate mixture of a known weight of the substance with soda-lime<sup>1</sup> in a glass tube, and collecting the ammonia in a bulb apparatus containing hydrochloric acid (fig. 4).

Ammonic chloride is then formed, which is estimated as ammonic-platinic chloride as follows :—

The hydrochloric solution is mixed with an excess of platinic

<sup>1</sup> Soda-lime is a mixture of sodic hydrate and calcic oxide (quick lime); it is infusible at a red heat, and is easily powdered, whereas sodic hydrate is easily fusible and extremely hygroscopic, and cannot therefore be intimately mixed with the substance.

chloride, and evaporated to dryness on the water-bath; the residue is treated with a mixture of alcohol and ether, which dissolves the excess of platinic chloride, leaving the ammonio-platinic chloride  $(\text{NH}_4)_2\text{PtCl}_6$ , which is collected on a tared filter, dried at  $100^\circ$ , and weighed; or the salt and its filter are carefully ignited in a crucible, and the amount of metallic platinum remaining determined.

Since  $(\text{NH}_4)_2\text{PtCl}_6 : \text{N}_2 = 446 : 28$   
 or  $\text{Pt} : \text{N}_2 = 197 : 28$

then, if  $x$  or  $y$  be respectively the weight of double salt, or of metallic platinum, obtained, the weight of nitrogen,  $\text{N}$ , contained in the weight of substance ( $w$ ) taken for analysis, is obtained by the following proportions:

$$\begin{aligned} 446 : 28 &= x : \text{N} \\ 197 : 28 &= y : \text{N} \end{aligned}$$

and the number of parts of nitrogen ( $\text{N}p$ ) contained in every 100 parts of the substance analysed by the proportion:

$$\text{N} : 100 = w : \text{N}p.$$

The amount of ammonia formed may also be determined by conducting it into a measured volume of sulphuric acid of known strength, and determining after the combustion by titration the amount of acid still unneutralised.

To determine nitrogen in compounds which do not evolve the whole of the nitrogen they contain as ammonia when heated with alkali (nitro-compounds, &c.), Dumas' volumetric method, which indeed is applicable in all cases, is employed.

The substance is intimately mixed with cupric oxide, as in the determination of carbon and hydrogen, and a roll of metallic copper is placed in the fore part of the tube; but before filling in the cupric oxide, a quantity of hydric sodic carbonate,  $\text{NaHCO}_3$ , or of a mixture of dry sodic carbonate and potassic dichromate, sufficient to occupy about six inches at the sealed end of the tube, is introduced. The tube is provided with a delivery tube, dipping under mercury (fig. 5). Before commencing the combustion, a portion of the hydric sodic car-

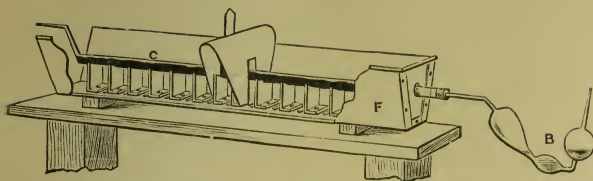


FIG. 4.—C, Combustion tube. F, Charcoal combustion furnace. B, Bulbs containing hydrochloric acid

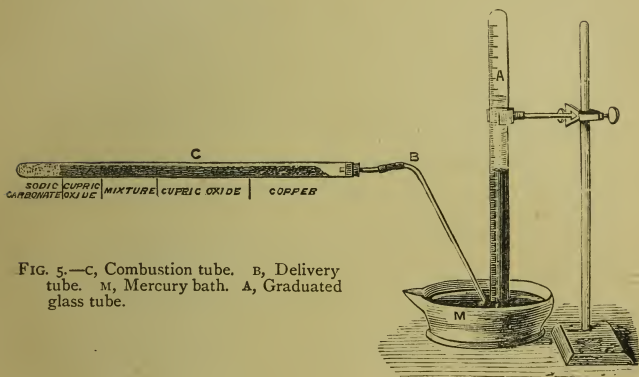


FIG. 5.—C, Combustion tube. B, Delivery tube. M, Mercury bath. A, Graduated glass tube.

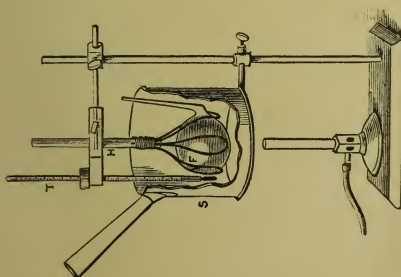


FIG. 6. Vapour-density determination by Dumas' method, p. 19.—F, Glass flask. H, holder. T, Thermometer. S, Saucepan containing heated liquid.

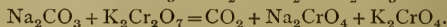
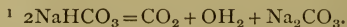
bonate, or of the chromate mixture, is heated : carbonic anhydride is evolved,<sup>1</sup> and expels the air from the tube. When the escaping gas is found, on testing, to be entirely absorbed by potassic hydrate solution, a graduated glass vessel, two-thirds filled with mercury and one-third with potassic hydrate solution, is inverted over the delivery tube, and the metallic copper and cupric oxide, and afterwards the mixture of substance and oxide, are heated to redness. The products of combustion, viz. carbonic anhydride and nitrogen, pass over into the graduated tube, where the former is absorbed by the potassic hydrate. At the close of the combustion, the remaining sodic carbonate is heated, and the whole of the nitrogen in the tube swept over by the current of carbonic anhydride. The tube is then transferred to a vessel of water, and the mercury and potassic hydrate solution are allowed to fall out and become replaced by water; it is then raised perpendicularly until the water in and outside are on a level, and the volume of nitrogen is read off, the temperature and pressure under which it is measured are also noted, and from these data the weight of nitrogen  $w$ , is calculated by the formula :

$$W = \cdot 0012566 v \frac{I}{I + \cdot 00367 t^{\circ}} \frac{B - f}{760}$$

in which  $v$  is the volume read off in cubic centimetres,  $t^{\circ}$  the temperature of the gas,  $B$  the height of the barometer in millimetres, and  $f$  the tension of aqueous vapour at the temperature  $t^{\circ}$ , expressed in millimetres of mercury. The constant  $\cdot 0012566$  is the weight in grammes of one cubic centimetre of nitrogen at  $0^{\circ}\text{C}$ . and under 760 mm. pressure.

*Determination of Oxygen.*—No simple method of estimating oxygen has been devised. It is usually estimated by difference, that is, by determining all the other elements present in the compound, and deducting the sum of their percentages from 100.

*Determination of Chlorine, Bromine, Iodine, Sulphur, and Phosphorus.*—These elements can seldom be detected





in organic bodies by the ordinary tests, but only after destroying the compound by ignition with an alkali or a metallic oxide, or by heating with concentrated nitric acid.

A variety of methods for determining these elements have been proposed, but one of the simplest is that devised by Carius.

A weighed quantity of the substance (·2–·3 grm.) is introduced, together with about 5 grms. of nitric acid (Sp. gr. 1·5)—and if the substance contain chlorine, bromine, or iodine, a few crystals of argentic nitrate—into a piece of combustion tube 15–18 inches long, securely sealed at one end. The open end is next drawn out to a point and sealed, and the tube is then heated in an oil-bath for 2–4 hours, at a temperature of 150°–300°, according to the nature of the substance. When cool, the point of the tube is carefully opened in the blow-pipe flame, the gas is allowed to escape, the top of the tube is cut off, and the contents washed into a beaker. Supposing the substance to have contained chlorine, bromine, or iodine and sulphur, or phosphorus, the argentic chloride, bromide, or iodide, is filtered off and weighed; the excess of silver in solution is precipitated by hydrochloric acid, the precipitate is removed by filtration; and the sulphur or phosphorus, present in the filtrate as sulphuric or phosphoric acid, may then be determined in the usual manner by precipitation as baric sulphate, or ammoniacal magnesian phosphate respectively.

Chlorine (bromine or iodine) may also be estimated by heating the substance to redness in a tube with pure quicklime, whereby calcic chloride (bromide, iodide) is formed. The contents of the tube are afterwards dissolved in dilute nitric acid, and the chlorine (bromine or iodine) precipitated as argentic chloride (bromide or iodide). Again, sulphur and phosphorus may be determined by fusing the organic substance with pure sodic hydrate and potassic nitrate, or by heating in a tube with sodic carbonate, or potassic chlorate. In all these cases a sulphate, or phosphate, is formed by the oxidation of the sulphur, or phosphorus, which is then estimated in the usual manner.

All other elements occasionally met with in organic compounds are determined by the ordinary methods, but usually after the organic character of the substance has been destroyed by ignition or oxidation.

#### EMPIRICAL FORMULÆ.

Having determined the percentage composition of an organic substance, it is easy to deduce the empirical formula, or simplest expression of the results of analysis in terms of the values represented by the symbols of the elements present in the compound.

The method is to divide the percentage numbers by the combining weights of the elements to which they refer, and afterwards to reduce the quotients to their simplest expression. The following examples may serve as illustrations:—

By analysis of acetic acid, it is found that 100 parts consist of

|                        |   |   |   |   |   |              |
|------------------------|---|---|---|---|---|--------------|
| Carbon                 | . | . | . | . | . | 39.96        |
| Hydrogen               | . | . | . | . | . | 6.74         |
| Oxygen (by difference) | . | . | . | . | . | <u>53.30</u> |
|                        |   |   |   |   |   | 100.00       |

By dividing these numbers respectively by the combining weights of carbon, hydrogen, and oxygen, thus—

$$\frac{39.96}{12} = 3.33; \quad \frac{6.74}{1} = 6.74; \quad \frac{53.30}{16} = 3.33,$$

numbers are obtained as quotients which, bearing in mind the unavoidable errors of experiment, evidently are in the proportion of 1 : 2 : 1; the empirical formula ( $\text{CH}_2\text{O}$ ) is therefore assigned to acetic acid.

Again, 100 parts of turpentine-oil contain

|          |   |   |   |   |   |              |
|----------|---|---|---|---|---|--------------|
| Carbon   | . | . | . | . | . | 88.20        |
| Hydrogen | . | . | . | . | . | <u>11.80</u> |
|          |   |   |   |   |   | 100.00       |

now  $\frac{88.20}{12} = 7.35; \quad \frac{11.80}{1} = 11.80.$



Dividing the quotient 11·80 by the quotient 7·35 ( $\frac{11\cdot80}{7\cdot35} = 1\cdot6$ ), it is found that for every unit weight of carbon, turpentine contains 1·6 unit weights of hydrogen, or 10 of carbon and 16 of hydrogen; consequently the simplest expression of the composition of a substance containing 88·20 per cent. of carbon and 11·80 per cent. of hydrogen is given by the formula  $C_5H_8$ .

If the numbers obtained by analysis were rigidly exact, there would evidently be no difficulty in determining the empirical formula of any compound, but since this is not the case, it is often necessary, in order to arrive at the true expression, not only to analyse the substance itself, but also to examine its behaviour under various conditions, and to prepare from it, if possible, and analyse, a series of derivatives. In all cases, to ascertain how far the empirical formula calculated is admissible, the percentage composition of a body having the formula deduced must be calculated and compared with the percentage numbers obtained by actual analysis; if the two agree within the limits of usual error of experiment, the formula may be accepted. For example, the percentage composition of narcotine as found by analysis is :

|          |   |   |   |   |                 |
|----------|---|---|---|---|-----------------|
| Carbon   | . | . | . | . | 63·78 per cent. |
| Hydrogen | . | . | . | . | 5·76   "   "    |
| Nitrogen | . | . | . | . | 3·32   "   "    |
| Oxygen   | . | . | . | . | 27·14   "   "   |
|          |   |   |   |   | <hr/> 100·00    |

from which the formula  $C_{22}H_{23}NO_7$  has been deduced. Calculating the percentages required by that formula as follows :—

|          |   |   |   |   |                      |
|----------|---|---|---|---|----------------------|
| Carbon   | . | . | . | . | $22 \times 12 = 264$ |
| Hydrogen | . | . | . | . | $23 \times 1 = 23$   |
| Nitrogen | . | . | . | . | $1 \times 14 = 14$   |
| Oxygen   | . | . | . | . | $7 \times 16 = 112$  |
|          |   |   |   |   | <hr/> 413            |

$$413 : 264 = 100 : 63.92$$

$$413 : 23 = 100 : 5.57$$

$$413 : 14 = 100 : 3.39$$

$$413 : 112 = 100 : 27.12$$

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$$100.00$$

it is evident that there is a fair agreement between the calculated and experimental numbers ; as is usual, the analysis shows a slight excess of hydrogen, and a slight deficiency of carbon.

#### MOLECULAR OR TWO-VOLUME FORMULÆ.

The formulæ generally employed to represent chemical compounds are what are termed molecular formulæ : on the atomic hypothesis they are regarded as expressing the absolute number of atoms of the various elements contained in the molecules, or least quantities capable of existing in the free state, of the compounds to which they refer.

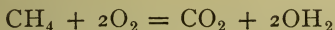
Apart from this hypothesis, however, the so-called molecular formula of a compound is, as a matter of fact, that formula which expresses the relative number of unit weights of the elements of which it is composed present in a volume of its vapour equal to the volume occupied by two unit weights of hydrogen *under the same conditions as to temperature and pressure*.

All formulæ constructed on this understanding therefore represent comparable quantities of the substances to which they refer taken in the gaseous state.

Thus the formula  $C_2H_4O_2$ , for acetic acid, represents that it is a compound of two unit weights, or  $12 \times 2$  parts, of carbon ; of 4 unit weights, or  $4 \times 1$  parts, of hydrogen ; and of 2 unit weights, or  $2 \times 16$  parts, of oxygen, the which 60 parts ( $24 + 4 + 32$ ) of acetic acid occupy in a gaseous condition the same volume as two parts of

hydrogen at the same temperature and under the same pressure.

If then it be agreed to consider the volume occupied by two parts by weight of hydrogen at any temperature and under any pressure as two volumes, the formulæ which represent the number of parts by weight of the substances to which they refer, which occupy in the gaseous state the volume of two parts by weight of hydrogen under like conditions as to temperature and pressure, may conveniently be termed two-volume formulæ. It is obvious that the equations in which these formulæ are made use of represent not only the number of parts by weight, but also the number of volumes in the gaseous state, of the agents and resultants. Thus the equation representing the combustion of marsh gas in oxygen :



conveys the information that sixteen parts by weight of marsh gas, or two volumes, burnt with sixty-four parts by weight, or four volumes, of oxygen, yield forty-four parts by weight, or two volumes, of carbonic anhydride, and thirty-six parts by weight, or four volumes, of water (gas).

The two-volume formula may be either identical with, or some simple multiple of, the empirical formula. For example, the empirical formula of turpentine (p. 13) is  $\text{C}_5\text{H}_8$ , but a determination of its *vapour density* shows that the number of parts by weight expressed by this formula only occupy the same volume as one part by weight of hydrogen ; therefore, in order that the formula may represent the quantity of turpentine which occupies two volumes, the empirical formula must be doubled, and thus it becomes  $\text{C}_{10}\text{H}_{16}$ .

Similarly the empirical formula deduced from the analysis of benzene is  $\text{CH}$ , but according to the vapour density determination,  $\text{C}_6\text{H}_6$  is the two-volume formula of benzene.

It is not always possible to determine directly the volume which any particular weight of a given compound will

occupy in the gaseous state, since many substances either cannot be volatilised, or suffer decomposition when converted into vapour. In such cases a variety of physical and chemical considerations have to be taken into account in determining the formula, such as the specific heat, specific gravity, and more especially the mode of formation of the compound; its behaviour under the influence of reagents; and its conversion into substitution derivatives. The acceptance of formulæ thus deduced, therefore, necessarily involves the assumption, that, could the substances be volatilised unchanged, the number of parts represented by the respective formulæ would occupy, in the gaseous condition, the same volume as two parts by weight of hydrogen at the same temperature and pressure.

Moreover, it is not always the formula deduced from the ascertained vapour density of the substance which is accepted as the true two-volume formula.

The compounds phosphorus pentachloride, sulphuric acid, and isoamylic iodide, for example, are always represented respectively by the formulæ  $\text{PCl}_5$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{C}_5\text{H}_{11}\text{I}$ , whereas according to experiment the amounts represented by each of these formulæ occupy in the gaseous state a greater volume than two parts of hydrogen at the same temperature and under the same pressure. But examination shows that when these bodies are converted into vapour, and heated above their boiling points, they are decomposed: thus  $\text{PCl}_5$  is converted into  $\text{PCl}_3 + \text{Cl}_2$ ;  $\text{H}_2\text{SO}_4$  into  $\text{SO}_3 + \text{OH}_2$ ;  $\text{C}_5\text{H}_{11}\text{I}$  into  $\text{C}_5\text{H}_{10} + \text{HI}$ .

The term *disassociation*, or *dissociation*, has been aptly applied to this decomposition of bodies by heat. Dissociation usually commences at, or a few degrees above, the boiling point of the compound; it is then only partial, however, but becomes more and more perfect as the temperature is raised, until finally the whole of the compound is decomposed. In the case of bodies, such as the above-mentioned, which split up into two others on heating, the

vapour then occupies double the space which it would fill if the compound volatilised without undergoing decomposition.<sup>1</sup>

It is not to be supposed that the vapour of a substance undergoing dissociation is in a quiescent state, or that the phenomenon consists merely in the simple progressive resolution of the compound into simpler bodies. There is little doubt that whilst portions of the compound are decomposed, a certain proportion of the products of decomposition recombine and reproduce the original compound; so that at any particular temperature below that at which decomposition is complete, the vapour consists of a mixture of the original compound with its products of decomposition, and it is only when the temperature has risen so high as entirely to overcome this tendency of the decomposition products to recombine—or, more strictly speaking, that the extent to which recombination takes place is exactly equalled by the extent to which decomposition is effected—that dissociation is complete.

<sup>1</sup> The following table shows the rate at which, according to experiment, phosphorus pentachloride is decomposed. Its boiling point is about 160°–165°; and the calculated density of its vapour referred to hydrogen as unity is  $104\cdot25 \left( \frac{31 + 5 \times 35\cdot5}{2} \right)$ , whilst the density of a mixture of equal volumes of phosphorus trichloride and chlorine is half as great, or 52·125.

| Temperature. | Vapour Density. | Percentage of Decomposition. |
|--------------|-----------------|------------------------------|
| 182°         | 76·2            | 41·7                         |
| 190°         | 72·0            | 44·3                         |
| 200°         | 70·0            | 48·5                         |
| 230°         | 62·0            | 67·4                         |
| 250°         | 57·7            | 80·0                         |
| 274°         | 55·4            | 87·5                         |
| 288°         | 52·9            | 96·2                         |
| 300°         | 52·6            | 97·3                         |

It is evident that the decomposition products of a compound can only be present in the vapour in such proportions that the amount of the one is exactly sufficient to reproduce the original compound if combined with the whole of the other; neither being in excess, the attraction between them is a minimum one. By increasing the proportion of the one to the other, it may be expected, however, that the tendency to recombine will be increased, and, indeed, that if a sufficient excess of the one be present, the original compound will be reproduced as rapidly as it is decomposed; so that practically the vapour would possess the same density as if the substance volatilised unchanged.

Conditions such as are required by these considerations are obtained when a mixture of phosphorus penta- and ter-chlorides, for example, is converted into vapour, and it is found that the density of the pentachloride thus determined closely corresponds to that required by the formula  $\text{PCl}_5$ . In this case, no doubt the chlorine momentarily set free by the decomposition of the pentachloride by heat, being in presence of a considerable excess of phosphorus terchloride, is able at once entirely to combine with it and to re-form the pentachloride.

The extension of this method of observation to those other compounds which dissociate, will probably in most, if not in all cases lead to like results.

This fact with regard to the behaviour of phosphorus pentachloride, added to the evidence afforded by its chemical behaviour, appears then thoroughly to justify the assumption that the observed vapour densities of such compounds as the above-quoted are abnormal, or, in other words, that the formulæ  $\text{PCl}_5$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{C}_5\text{H}_{11}\text{I}$ , &c., are really those which denote the relative weights of these substances which would form two volumes of vapour, could they be volatilised unchanged.



## DETERMINATION OF VAPOUR DENSITY.

From the foregoing it is evident that the determination of the vapour density, or specific gravity of the vapour, of a compound is a most important operation. Two methods are in use—Dumas' and Gay Lussac's. By the first the weight of a given volume of the vapour is determined; by the second the volume which a given weight of the substance occupies in the gaseous state is ascertained.

*Dumas' method.*—The neck of a light glass flask, from 50 to 300 cubic centimetres in capacity, according to the nature of the substance, and the amount at the disposal of the operator, is softened in the blow-pipe flame and drawn out to a fine point, as represented in fig. 6. After the weight of the perfectly clean dry flask has been ascertained—the atmospheric temperature, and the height of the barometer at the moment of weighing are carefully noted—from 5 to 10 grms. of the substance are introduced by warming the flask, and then plunging the point into the liquid,<sup>1</sup> which is forced upwards as the vessel cools. The flask is then plunged, point upwards, into a bath of water, oil, or fusible metal, heated to the required temperature. The liquid is rapidly converted into vapour, which, if sufficient substance be employed, expels the whole of the air from the flask; so soon as vapour ceases to issue, and the temperature of the bath is constant, the fine point is hermetically sealed by the application of a blow-pipe flame, and simultaneously the temperature of the bath and the height of the barometer are noted. After cooling, the flask is cleansed externally, and again weighed—the operator noting at the same time the temperature and the height of the barometer; the point of the neck is then broken off under mercury, or water recently boiled and allowed to cool out of contact with the air; the mercury, or water, rushes into the globe, owing to the vapour being condensed, and, if all the air have been expelled, completely fills the flask. By measuring or weighing afterwards the amount of mercury or water which thus enters, the capacity

<sup>1</sup> Solids are introduced before the neck of the flask is drawn out.

of the flask is ascertained. If the flask contain air, it will not be entirely filled; the volume of the air which remains is then determined by refilling the flask entirely with mercury or water, after the amount which first enters has been ascertained, and again weighing or measuring. The difference between the two measurements represents the volume of air retained in the flask.

It is in all cases advisable to heat the vapour to a temperature considerably above the boiling point of the substance, since the vapours of most compounds act only as perfect gases at temperatures some distance from their condensing points. For example, acetic acid, which boils at  $117^{\circ}$ , has at temperatures near to its boiling point a vapour density one and a half times as great as at  $250^{\circ}$  and upwards, as is evident from the following table :

|                |               |               |               |               |               |               |               |
|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Temperature    | $125^{\circ}$ | $130^{\circ}$ | $140^{\circ}$ | $160^{\circ}$ | $190^{\circ}$ | $250^{\circ}$ | $300^{\circ}$ |
| Vapour density | 46.1          | 45.0          | 41.8          | 35.7          | 33.1          | 30.01         | 30.01.        |

Few compounds, however, are so exceptionally abnormal in this respect as acetic acid.

The data obtained in the above manner, from which the density ( $D$ ) is calculated are :

(1) The weight ( $w$ ) of the flask filled with air at the temperature  $t^{\circ}$  and pressure  $p$ .

(2) The weight ( $w'$ ) of the flask filled with the vapour of the substance at the temperature  $t'^{\circ}$  and pressure  $p'$ .

(3) The capacity ( $v$ ) of the flask in cubic centimetres.

In order to ascertain the weight ( $w^{\circ}$ ) of the vacuous flask, the weight of air ( $w$ ) which it contains must be deducted from the weight of the flask filled with air :

$$w^{\circ} = w - w$$

now 1 c.c. of air at  $0^{\circ}\text{C.}$  and 760 mm. weighs .001293 gm. ; hence :

$$w = .001293 \frac{v \times 273 \times p}{273 + t^{\circ} \times 760} \text{ or } w = .001293 \frac{v \times 273 \times 760}{273 + t^{\circ} \times p}$$

according as  $p$  is greater or less than 760 mm.

Deducting the weight of the vacuous flask ( $w^{\circ}$ ) from



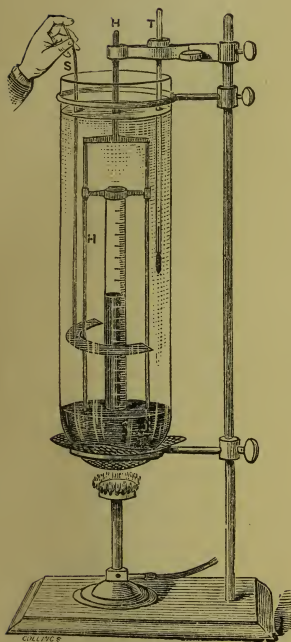


FIG. 7. Vapour-density determination by Gay-Lussac's method.—H, Tube-holder. T, Thermometer. S, Stirrer.

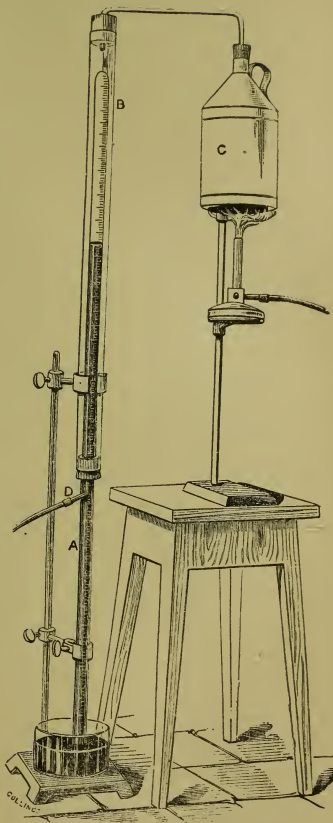


FIG. 8. Vapour-density determination by Hofmann's method.—A, Graduated glass tube. B, Glass jacket. C, Vessel containing boiling alcohol, water, or aniline. D, Tube leading to condenser.

the weight of the flask filled with vapour ( $w'$ ), the weight of substance ( $s$ ), which in the state of vapour at the temperature  $t^{\circ'}$  and pressure  $p'$  occupies the volume  $v$ , is ascertained.

$$s = w' - w^{\circ}$$

Since the density referred to hydrogen is required, the weight ( $H$ ) of an equal volume ( $v$ ) of hydrogen at the same temperature ( $t^{\circ'}$ ) and pressure ( $p'$ ) must then be ascertained: now 1 c.c. of hydrogen at  $0^{\circ}$  and 760 mm. weighs  $\cdot 0008936$  gm. ; therefore :

$$H = \cdot 0008936 \frac{v \times 273 + t^{\circ'} \times p'}{273 \times 760} \text{ or } \cdot 0008936 \frac{v \times 273 + t^{\circ'} \times 760}{273 \times p'} \quad (1) \qquad (2)$$

according as  $p'$  is greater or less than 760 ; hence :

$$D = \frac{s}{H}$$

In accurate experiments a correction must be made for the expansion on heating, and consequent change of capacity, of the flask ; also for the errors of the mercurial thermometer, and moreover, allowance must be made if the temperature and pressure at the second weighing are different from the temperature and pressure at the time of first weighing the flask filled with air.

If the air be not wholly expelled from the flask by the vapour, the volume ( $v$ ) of this residual air at the temperature  $t^{\circ'}$  and pressure  $p'$  must be deducted from the capacity of the flask ( $v$ ), and  $v-v$  substituted for  $v$  in the last of the above formulæ, in calculating the weight of the volume of hydrogen which occupies the same space as the vapour of the substance, which, in such a case, of course has the volume  $v-v$ .

It was usual formerly to refer the vapour density to air as unity. To convert the density referred to air into the density referred to hydrogen, divide by  $\cdot 0693$ , the specific gravity of hydrogen referred to air as unity.

Dumas' method is not only applicable to all compounds whose boiling points are within the range of the mercurial thermometer, but to volatile compounds generally, whatever the boiling point. In these cases the flask is heated in the vapour of a substance of known boiling point, such as mercury, (B.P.  $350^{\circ}$ ), sulphur (B.P.  $440^{\circ}$ ), cadmium (B.P.  $860^{\circ}$ ), or zinc, (B.P.  $1040^{\circ}$ ). Glass flasks may be employed with the two former, but in the other cases flasks of porcelain must be used. With such vessels Deville and Troost have even made determinations at the high temperature of a wind furnace; placing in the furnace, in order to determine the temperature, a second flask containing iodine. After the experiment the amount of iodine remaining in the flask was estimated, and the rate of expansion of iodine vapour, and the capacity of the flask, and the rate of expansion of its substance, being known, it was easy to calculate from these data the temperature to which the flasks had been exposed.

*Gay Lussac's method.*—The weighed quantity of substance enclosed in a thin glass bulb is introduced into a short graduated tube filled with mercury, which is supported in an iron cup containing mercury, and plunged into a cylindrical glass bath filled with heated water, oil, or paraffin (fig. 7); the glass bulb is soon burst by the expansion of the contained substance, and the tube becomes partly filled with vapour. When the temperature is sufficiently high and constant, the volume of the vapour and the temperature to which it is heated are noted, as well as the height of the column of mercury in the tube, the height of the column of water, or oil, pressing on the base of the column of mercury, and the atmospheric pressure as registered by the barometer. From these data the vapour density may be readily calculated.

Gay Lussac's method is only available for substances whose boiling points are considerably below that of mercury. It has the advantage over Dumas', however, of requiring but a small quantity of substance.

A most valuable modification of this method has lately been devised by Professor Hofmann, who employs (fig. 8) a

graduated glass tube closed at one end, about 1,000 mm. in length and 15–20 mm. in width, which is filled with mercury, and the open end inverted in a vessel containing mercury. It is surrounded by a cylindrical glass jacket, through which, according to the temperature at which the determination is to be made, a current of the vapour of boiling alcohol, water, aniline, or some other substance of constant boiling point, is urged, whereby the substance previously introduced into the tube in a minute stoppered glass bottle is converted into vapour. The volume which the vapour occupies, the temperature to which it is heated, the height of the mercury column in the tube, and the atmospheric pressure<sup>1</sup> are noted; the weight of a quantity of hydrogen which at the same temperature and under the same pressure would occupy the same volume as the vapour of the amount of substance taken is then calculated, and by dividing this weight of hydrogen into the weight of substance taken, the vapour density of the substance in question is ascertained.

The boiling points of all substances are considerably lowered by a reduction of pressure, and not only so, but the tendency to decompose which many exhibit at temperatures close to the boiling point, under ordinary pressures, is greatly lessened. Now it is evident that when the tube is inverted as above described, there will be a considerable empty space at the top; into this the substance volatilises, and is converted into vapour under reduced pressure, and therefore at a temperature much lower than its boiling point under ordinary conditions; for example, the vapour density of aniline, which boils at 182° under a pressure of 760 mm. of mercury, may be in this way determined by heating the tube by the vapour of boiling water (100°); hence the great value of this method and its superiority over Gay Lussac's.

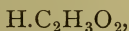
<sup>1</sup> The mercury column in the tube balances a certain proportion of the atmospheric pressure, hence the pressure on the vapour is equal to the difference between these two measurements.

## RATIONAL FORMULÆ.

By common consent, the arrangement of the elementary symbols composing the two-volume formulæ of chemical compounds in certain ways is understood to imply certain facts with regard to the nature and properties of the compounds represented, and more especially with regard to the modes in which they are formed, and in which they undergo decomposition. Formulæ which fulfil these conditions are termed rational formulæ ; they constitute, in fact, the chemist's shorthand, and it behoves the student therefore early to become acquainted with the meaning attached to the various arrangements of symbols in common use.

The following instances will serve to render the functions of rational formulæ more intelligible, and also to show that several rational formulæ may be employed to represent one and the same compound, according to the amount of information it is desired to convey.

1. Thus we write acetic acid, whose two-volume formula is  $C_2H_4O_2$ ,



and mean to express thereby that it is a *monobasic* acid, or one in which one unit weight of hydrogen is replaceable by the equivalent quantity of a metal, such as sodium, silver, &c., to form such salts as sodic acetate,  $NaC_2H_3O_2$ , or argentic acetate,  $AgC_2H_3O_2$ . This convention of placing one or more units of hydrogen apart on the left of the formula is generally applied to the acids, it being agreed to denote the *basicity* of an acid, i.e. the number of units of hydrogen replaceable by metals which it contains, by the number of units of hydrogen written to the left of the point.

2. A second more developed rational formula for acetic acid is



which has reference to such reactions as that which occurs

between this acid and phosphorus pentachloride, represented by the following equation :

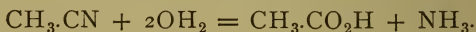


and one of the meanings to be attached to any formula in which the (OH) or hydroxyl-group, as it is termed, figures is that when the body represented is acted upon by  $\text{PCl}_5$  it will exchange (OH) for Cl.

3. By certain means one proportion of hydrogen in marsh gas (methane),  $\text{CH}_4$ , may be replaced by iodine, forming iodomethane,  $\text{CH}_3\text{I}$ , which, by the action of potassic cyanide, is converted into cyanomethane,  $\text{CH}_3(\text{CN})$  ; if this body be heated with water in presence either of acids or alkalies, it is resolved into acetic acid and ammonia. Conformably to this mode of formation of acetic acid, its formula may be written



and the reaction is expressed by the equation :

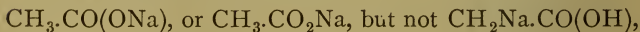


4. Lastly, by reason of the reaction with phosphorus pentachloride, the group  $\text{CO}_2\text{H}$  is resolved into  $\text{CO}(\text{OH})$ , so that the formula becomes

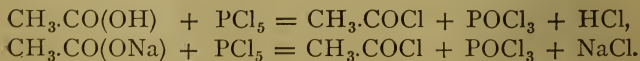


and it is found that all the various reactions in which acetic acid takes part are capable of representation by this formula.

Then we write sodic acetate :



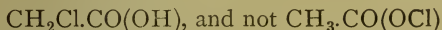
because it is found that when acted upon by  $\text{PCl}_5$  (ONa) is removed and replaced by chlorine, just as (OH) is in acetic acid :





And since the other salts of acetic acid exhibit a precisely similar behaviour, they are represented generally by such formulæ as  $\text{CH}_3\cdot\text{CO}_2\text{M}'$  and  $(\text{CH}_3\cdot\text{CO}_2)_2\text{M}''$ , &c., in which  $\text{M}'$  and  $\text{M}''$  denote monad and dyad metals respectively.

Again, monochloracetic acid, the first product of the action of chlorine on acetic acid, is written :



because we find that it exchanges (OH) for Cl when acted upon by  $\text{PCl}_5$  ; thus :



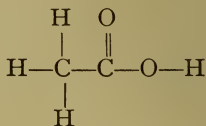
In short, the employment of such a group of symbols as (CO.OH) as part of a formula denotes that the compound represented will, when treated by certain reagents, be affected in certain ways : that it will form metallic salts ; that it will exchange OH for Cl when acted upon by  $\text{PCl}_5$  ; that it may be obtained probably from a body bearing to it the same relation that acetic acid,  $\text{CH}_3\cdot\text{CO}_2\text{H}$ , bears to methane,  $\text{CH}_4$ , by replacing hydrogen in that body by iodine, this in turn by cyanogen, (CN), and heating the product with water, &c.

Rational formulæ, such as the above, are frequently termed constitutional formulæ, and by some structural formulæ. The use of these terms seems to imply, however, that such formulæ express the constitution, or structure, of the bodies to which they refer ; but we must guard ourselves most carefully against this impression, since, hypothesis aside, we possess no real knowledge as to the internal constitution of chemical compounds, or of the mode of arrangement of the atoms of which bodies are presumed to be made up, and although rational formulæ *may* represent the proximate constitution of chemical compounds, yet in the present state of our knowledge it is advisable to regard them simply as condensed symbolic expressions of the chemical nature and mode of formation of the compounds represented : they



enable us, so to speak, to decipher at a glance the chemical history of compounds.

*Graphic formulæ* are a still more developed form of rational formulæ. For example, the graphic formula for acetic acid is



Here the fact that tetrad carbon is capable of uniting with four unit weights of monad hydrogen (as in marsh gas,  $\text{CH}_4$ ), or with two unit weights of dyad oxygen (as in carbonic anhydride,  $\text{CO}_2$ ), is represented by the four lines proceeding from the elementary symbol C; similarly dyad oxygen is represented by the elementary symbol O, with two lines; monad hydrogen by H, with one line. This formula, therefore, to a certain extent necessarily assumes that in acetic acid one atom of tetrad carbon is directly united with three atoms of monad hydrogen, and also to a second atom of carbon, with which one atom of dyad oxygen is wholly, the second atom partially united, the latter being in union with an atom of hydrogen.

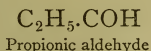
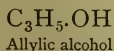
#### POLYMERISM, METAMERISM, ISOMERISM.

1. Bodies of the same percentage composition, but of different vapour densities, are termed *polymeric*. Thus *aldehyde*,  $\text{C}_2\text{H}_4\text{O}$ , is polymeric with *paraldehyde*,  $\text{C}_6\text{H}_{12}\text{O}_3$ —forty-four parts of aldehyde vapour and 132 ( $44 \times 3$ ) parts of paraldehyde vapour each occupy the same volume as two parts of hydrogen under like conditions of temperature and pressure. The unit weights of polymeric compounds are always different simple multiples of the same empirical formula, the unit weight of a compound being the sum

of the unit weights of its constituents, each multiplied by the suffix which indicates the number of unit weights present in two volumes of vapour. Thus the unit weight of acetic acid,  $C_2H_4O_2$ , is sixty ( $12 \times 2 + 1 \times 4 + 16 \times 2$ ), and it is always in that proportion, or some simple multiple thereof, that acetic acid enters into reaction with other substances.

2. Bodies of the same percentage composition and same vapour density, which exhibit differences, more or less marked, in physical properties, but which behave in nearly all cases dissimilarly when acted upon by the same reagents, are said to be metameric. The three compounds, allylic alcohol, propionic aldehyde, and acetone, each represented by the undeveloped rational formula  $C_3H_6O$ , are thus related: the first is entirely decomposed on oxidation; the second yields propionic acid,  $C_3H_6O_2$ , when similarly treated; whilst the third is resolved into formic and acetic acids.

The developed rational formulæ which we are led to assign to these compounds are also, as a comparison will show, very different; thus:



3. Two or more bodies of the same percentage composition and same vapour density, which differ to a greater or less extent in physical properties (boiling point, specific gravity, &c.), and which either exhibit a similar behaviour under the influence of certain reagents, or, by their immediate formation from, or conversion into, the same compound, are shown to be members of the same series of compounds, are termed *isomeric*. The products obtained from isomeric bodies by various reactions are themselves frequently isomeric; thus the four isomeric butylic alcohols,  $C_4H_9(OH)$ , yield four isomeric butylic chlorides, bromides, or iodides when acted upon by hydrochloric, hydrobromic, or hydriodic

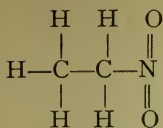
acid; the differences in boiling point and specific gravity which these derivatives exhibit among themselves are in the same sense as those which exist among the isomeric alcohols; thus the butylic alcohol of highest boiling point yields a chloride, bromide, or iodide of higher boiling point than either of the corresponding derivatives from the isomeric alcohols.

Isomeric compounds, however, do not always give rise to similar reactions under the influence of all reagents; thus the isomeric alcohols above cited behave very differently on oxidation: for example, one is converted into butyric acid,  $C_4H_8O_2$ ; a second into isobutyric acid,  $C_4H_8O_2$ ; a third into ethylmethylketone,  $C_4H_8O$ ; the fourth into a mixture of acetic and formic acids. Even in those reactions in which they are similarly affected, isomeric compounds exhibit differences more or less marked, more especially in the relative degrees of ease with which they enter into reaction: the one is invariably acted upon more readily than the other.

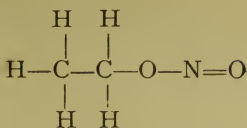
On the hypothesis that chemical compounds are composed of small indivisible particles, or atoms, it may be assumed that two or more bodies are isomeric or metameric, because certain of the atoms in the one occupy relatively different positions to those they occupy in the other, and this is the explanation usually given of isomerism and metamerism. Thus the two metameric compounds *nitroethane*, and *ethylic nitrite*, represented by reason of their chemical behaviour by the formulæ

Nitroethane,  $C_2H_5(NO_2)$ ; Ethylic nitrite,  $(C_2H_5O)ON$

may be supposed to differ owing to the circumstance that in the one the nitrogen is in direct union with the carbon, whereas in the other the carbon and nitrogen are held together, as it were, by oxygen, as expressed by the following graphic formulæ:



Nitroethane



Ethylic nitrite

The extreme readiness with which the nitrogen may be separated from the latter compound, and the difficulty of removing it from the former, is generally regarded as strong evidence in favour of this assumption as to the probable cause of the difference which exists between the two bodies.

Although such an apparently satisfactory explanation of the phenomena in question may thus be given, yet there are a considerable number of facts which tend to show that this explanation must be regarded with more or less mistrust.

The phenomenon of isomerism—and of metamerism—is unquestionably intimately connected with the amount of heat evolved in the reactions giving rise to the formation of isomerides. Whatever the ultimate constitution of chemical compounds may be, it is a fact that their formation is invariably accompanied by the evolution (in a limited number of cases by the absorption) of heat, which to our senses is evidence that there has been a transformation of energy, until then potential, into actual energy. Moreover, there is little doubt that in the formation of isomeric bodies from the same parent compound different amounts of heat are evolved; if so, the energies of the resulting compounds are assuredly different.

The production of isomerides by different series of reactions is, then, probably to be accounted for by the circumstance that different amounts of heat are evolved in the several series of reactions, so that finally bodies possessing different energies are formed. This supposition, that isomeric (and metameric<sup>1</sup>) compounds are bodies

<sup>1</sup> The difference between isomeric and metameric compounds is probably one of degree only, and not of kind, as usually assumed.

which, having the same composition, yet possess different energies, would also serve to explain their different behaviour under the influence of reagents. There is reason to believe that, of two isomerides, that of higher energy would in most cases enter into reaction more readily than that of lower energy, just as chlorine, an element of high energy—which in combining with hydrogen liberates a far greater amount of heat than do either bromine or iodine—is a far more energetic reagent than either of these.

Hitherto but little attention has been paid to this field of enquiry, which the study of the thermic phenomena accompanying chemical reactions affords. In it, however, undoubtedly lies hidden the explanation of many at present obscure problems in chemical science.

## CHAPTER II.

### CLASSIFICATION OF CARBON COMPOUNDS.

THE unit weight (twelve parts) of carbon is capable of uniting with at most four unit weights of hydrogen or other monad elements. The simplest known hydride of carbon has the composition  $\text{CH}_4$ , and is incapable of combining with chlorine, bromine, &c., being what is termed a *saturated* compound, but may exchange the whole or part of its hydrogen for an equivalent quantity of another element. Carbonic anhydride,  $\text{C}'''\text{O}''_2$ , hydrocyanic acid,  $\text{H}'\text{C}'''\text{N}'''$ , and cyanogen chloride,  $\text{Cl}'\text{C}'''\text{N}'''$ , are compounds which may be thus regarded as *substitution*-derivatives of the first hydride of carbon.

In the following, certain of these simpler compounds, which may thus be regarded as derived from the first hydride of carbon, will be shortly described before proceeding to the consideration of the hydrides themselves.

While the number of unit weights of any of the elements other than carbon, associated together in their various compounds, is, as a rule, extremely limited, seldom exceeding five, the number of unit weights of carbon contained in carbon compounds is often very great. It is this fundamental property of uniting with itself, so to speak, in a large number of different multiple proportions, which sharply distinguishes carbon from the other elements, and which appears to be the cause of the great multiplicity of its derivatives. With regard to the maximum combining power of these aggregates consisting of several unit weights of carbon, it is found that two unit weights are never associated with more than six, three with more than eight, or four with more than ten unit weights of hydrogen or other monads ; in short, that each addition of one unit weight of carbon raises the combining power by at most two monad units, so that the maximum combining power of an aggregate of  $n$ -units of carbon with monad elements is equal to  $2n + 2$ . The composition of the compounds of carbon and hydrogen containing the greatest possible amount of the latter element is therefore expressed by the general formula,  $C_nH_{2n+2}$ . It is from the *hydrocarbons*, as such compounds of carbon and hydrogen are termed, of this composition that more or less directly, as will be shown in the following pages, the remaining families of organic compounds may be built up ; they are therefore of paramount importance.

Besides these saturated hydrocarbons others are known containing proportionately less hydrogen ; these are capable of existing in the free state, and are termed *non-saturated* hydrocarbons, owing to their possessing the property of uniting directly, more or less readily, with certain elements, to form either saturated compounds of the  $C_nH_{2n+2}$  type, or intermediate compounds. They invariably differ from the corresponding terms of the  $C_nH_{2n+2}$  series by an even number of unit weights of hydrogen, and are



obtained from the members of that series by withdrawing from them one or more pairs of unit weights of hydrogen. This withdrawal of hydrogen may be effected in a large number of cases by the simple action of heat, the tendency thus to part with hydrogen becoming greater the higher up we go in the series.

Hydrocarbons differing from those of the  $C_nH_{2n+2}$  series by an uneven number of unit weights of hydrogen are not known; in all cases where their production might be expected, compounds are obtained which may be regarded as formed by the union of two such hydrocarbons. For example, if iodomethane,  $CH_3I$ , be treated with metallic sodium, iodine is withdrawn from it; we do not obtain methyl,  $CH_3$ , however, but the hydrocarbon,  $C_2H_6$  (ethane), thus :



Similarly a mixture of the two iodides,  $CH_3I$  and  $C_3H_5I$ , yields the hydrocarbon butylene,  $C_4H_8$ .

The general terms of the series of hydrocarbons of which up to the present time members have been obtained and investigated are as follows :—

|                |                |
|----------------|----------------|
| $C_nH_{2n+2}$  | $C_nH_{2n-14}$ |
| $C_nH_{2n}$    | $C_nH_{2n-16}$ |
| $C_nH_{2n-2}$  | $C_nH_{2n-18}$ |
| $C_nH_{2n-4}$  | $C_nH_{2n-22}$ |
| $C_nH_{2n-6}$  | $C_nH_{2n-24}$ |
| $C_nH_{2n-8}$  | $C_nH_{2n-26}$ |
| $C_nH_{2n-10}$ | $C_nH_{2n-32}$ |
| $C_nH_{2n-12}$ |                |

Each of these groups differs from the group next below, in that it contains two units of hydrogen more. Series thus related are termed *isologous* series. The members of each group form a *homologous* series, the successive terms of which differ by  $CH_2$  (see p. 70).

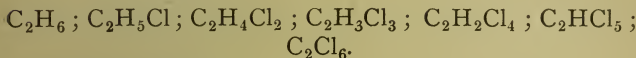
The various families of organic compounds considered in



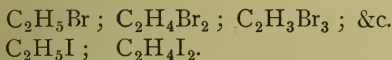
their relations to the above-mentioned hydrocarbons may conveniently be arranged in the following classes :—

I. *Hydrocarbons and their haloid Derivatives*.—One or more unit weights of chlorine, bromine, or iodine may be substituted either directly or indirectly for the equivalent quantity of hydrogen in the various hydrocarbons. For example, *methane*,  $\text{CH}_4$ , and *ethane*,  $\text{C}_2\text{H}_6$ , yield the following series of chlorinated derivatives :—

|                 |                          |                            |                        |                          |
|-----------------|--------------------------|----------------------------|------------------------|--------------------------|
| $\text{CH}_4$ ; | $\text{CH}_3\text{Cl}$ ; | $\text{CH}_2\text{Cl}_2$ ; | $\text{CHCl}_3$ ;      | $\text{CCl}_4$ .         |
| Methane.        | Monochloro-<br>methane.  | Dichloro-<br>methane.      | Trichloro-<br>methane. | Tetrachloro-<br>methane. |



Similarly we have :



All such hydrocarbon derivatives are termed haloid derivatives. Closely allied to them are several series of compounds which are conveniently regarded as derived from the hydrocarbons by the replacement of hydrogen by the monad groups  $(\text{CN})'$  ;  $(\text{SCN})'$  ;  $(\text{NO}_2)'$  ; or  $(\text{NH}_2)'$  ; e.g. :

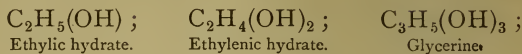
|                                      |                                                    |                                       |                                       |
|--------------------------------------|----------------------------------------------------|---------------------------------------|---------------------------------------|
| $\text{CH}_3(\text{CN})$ ;           | $\text{C}_2\text{H}_5(\text{SCN})$ ;               | $\text{C}_6\text{H}_5(\text{NO}_2)$ ; | $\text{C}_6\text{H}_5(\text{NH}_2)$ . |
| Cyanomethane.<br>(Methylic cyanide.) | Sulphocynoethane.<br>(Ethylic sulpho-<br>cyanate.) | Nitrobenzene.                         | Amidobenzene.                         |

Many of these are formed from the haloid derivatives of the hydrocarbons by double decomposition ; for example, cyanomethane is obtained by the action of potassic cyanide on iodomethane :

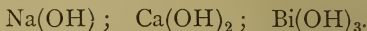


II. *Alcohols*.—The alcohols may be regarded as the hydroxyl  $(\text{OH})'$  substitution derivatives of the hydrocar-

bons, and are in all respects the organic analogues of the metallic hydrates ; thus we have :

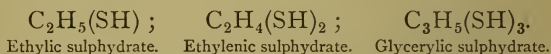


analogues of :



The modes of formation of the alcohols from the corresponding haloid derivatives of the hydrocarbons are, as will be seen later on, strictly analogous to the methods by which the metallic hydrates are obtained from the metallic chlorides, &c.

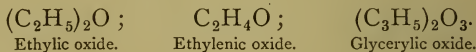
Closely related to the alcohols, and corresponding to the metallic sulphydrates, are a class of bodies termed *thio-alcohols*, or *mercaptans* ; e.g. :



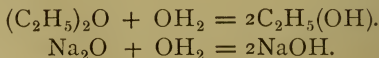
corresponding to :



III. *Ethers*.—The ethers are the *anhydrides* of the alcohols, to which they bear the same relation as the metallic oxides to the corresponding hydrates ; e.g. :



The ethers are more or less readily converted into alcohols by heating with water or alkalies, just as, under similar conditions, the metallic oxides are converted into hydrates :



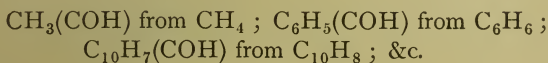
Analogues of the metallic sulphides are also included in this class ; for example :

analogous to  $(C_2H_5)_2S$  ;  $C_2H_4S$  ;  
 $Na_2S$  ;  $CaS$ .

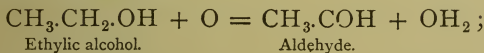
And also polysulphides such as

$(C_2H_5)_2S_2$  and  $(C_2H_5)_2S_3$   
 corresponding to  
 $Na_2S_2$  and  $Na_2S_3$ .

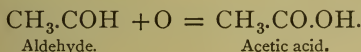
IV. *Aldehydes*.—The aldehydes are a class of bodies intermediate between the alcohols and the acids. They may be conveniently formulated as hydrocarbon derivatives in which the group  $(C^{iv}O''H)'$  replaces hydrogen ; thus we have :



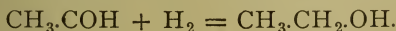
The aldehydes are formed by the oxidation of the corresponding alcohols, thus :



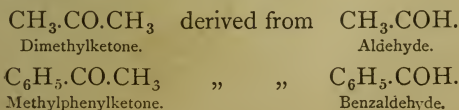
and on further oxidation are converted into acids containing the same number of unit weights of carbon :



On the other hand the aldehydes are readily transformed into alcohols by the action of nascent hydrogen :

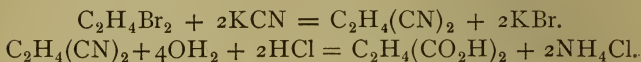


V. *Ketones*.—These compounds are closely related to the aldehydes, and may be regarded as derived from them by the replacement of hydrogen in the  $(COH)$  group by monad hydrocarbon groups ; thus we have :



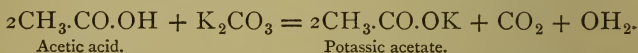
The ketones do not yield acids containing the same number of unit weights of carbon on oxidation ; hence they are readily distinguished from the aldehydes.

VI. *Acids*.—The acids are formed from the hydrocarbons by a series of operations, the final result of which may be said to be the substitution of hydrogen in the latter by the monad carboxyl <sup>1</sup> group ( $\text{CO}_2\text{H} = \text{CO.OH}$ ) ; thus we have succinic acid,  $\text{C}_2\text{H}_4(\text{CO}_2\text{H})_2$ , formed from ethane,  $\text{C}_2\text{H}_6$ , by the following series of reactions :



The acids furnish a numerous series of characteristic derivatives, namely : *metallic salts*, *haloid salts*, *ethereal salts*, *acid chlorides* (*bromides*, *iodides*, &c.), *amides*, and *haloid derivatives* and allied compounds.

The *metallic salts* are the characteristic products of the action of metallic oxides, hydrates, and carbonates on the acids ; e.g. :

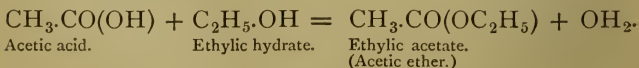


The *haloid salts* may be regarded as derived from the metallic salts by the replacement of the metal by chlorine, bromine, &c. ; thus the following haloid salts of acetic acid are known :



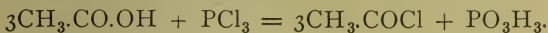
These compounds are all extremely unstable, and are never obtained by the direct action of the halogens on the acids (*infra*).

*Ethereal salts*, or compound ethers, are formed when the acids are acted upon by the analogues of the metallic hydrates, the alcohols ; thus :

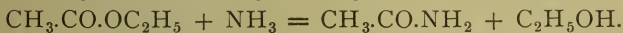


<sup>1</sup> From carbonyl (CO), hydroxyl (OH).

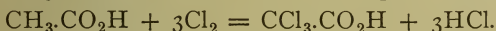
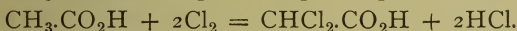
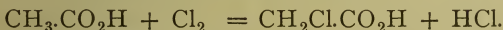
The *acid chlorides* (bromides, iodides) are the products of the action of the haloid phosphorus compounds on the acids, or their metallic salts :



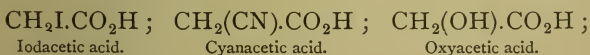
The *amides* are formed by the action of ammonia on the acid chlorides, or on the ethereal salts, or by distillation of the ammonium salts of the acids :



The *haloid derivatives*, which are mostly compounds of considerable stability, are formed by the direct action of chlorine, or bromine on the acids ; thus :



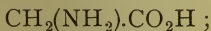
From many of the haloid derivatives a series of closely allied compounds may be obtained by double decompositions, such as :



Iodacetic acid.

Cyanacetic acid.

Oxyacetic acid.

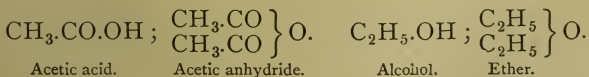


Amido-acetic acid.



Sulphacetic acid.

VII. *Anhydrides*.—These compounds bear the same relation to the acids that the ethers bear to the alcohols :



Acetic acid.

Acetic anhydride.

Alcohol.

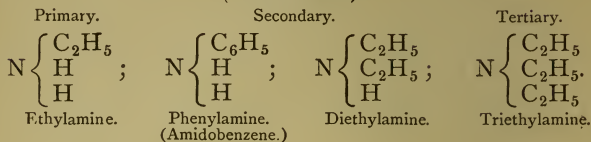
Ether.

They are reconverted into acids by the action of water.

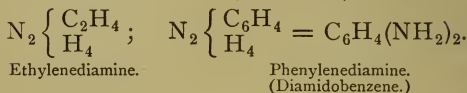
VIII. *Amines*.—The amines are a class of bodies which are generally regarded as derived from ammonia by the

substitution of hydrocarbon groups for hydrogen ; the following are examples of such compounds :—

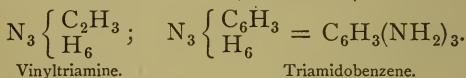
(*Monamines.*)



(*Diamines.*)

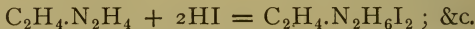
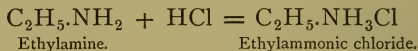


(*Triamines.*)

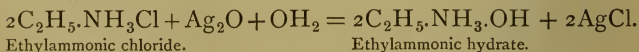


It is evident, however, that the primary amines may equally well be regarded as derived from the hydrocarbons by the substitution of  $n(\text{NH}_2)$  for  $n\text{H}$ .

These *organic ammonias* closely resemble ammonia in their properties : they combine directly with acids, forming substituted ammonium salts :

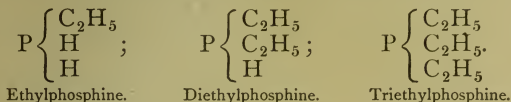


By treating these salts with moist argentic oxide the corresponding hydrates are obtained :

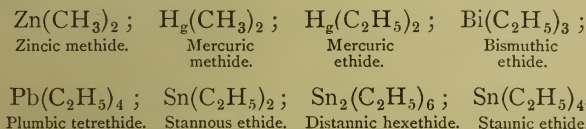


These hydrates are highly caustic bodies, and indeed exhibit throughout the behaviour of their inorganic analogues, the caustic alkalies, precipitating metals from their solutions as hydrates, &c.

The analogues of ammonia, *phosphine*,  $\text{PH}_3$ ; *stibine*,  $\text{SbH}_3$ ; and *arsine*,  $\text{AsH}_3$ , also yield derivatives corresponding to the primary, secondary, and tertiary monamines; e.g.:



IX. *Organo-metallic Compounds*.—These may be regarded as compounds of the metals with monad hydrocarbon groups; thus the following bodies are known among others:



A large number of carbon compounds are known, however, which cannot at present be included in either of the above series, as we are entirely unacquainted with their genetic relations to the hydrocarbons.

## CHAPTER III.

### GENERAL ACTION OF REAGENTS ON CARBON COMPOUNDS.

THIS chapter contains an outline description of the action of the more important reagents which the chemist employs in the study and elucidation of the chemical nature of carbon compounds.

*Action of Chlorine, Bromine, and Iodine*.—There is merely a difference of degree between the action exerted by chlorine and by bromine, chlorine being the more energetic reagent—because, we usually say, of its superior affinity for hydrogen. The behaviour of iodine is in many cases pecu-

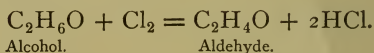


liar. The following modes of action of chlorine and bromine are to be distinguished.

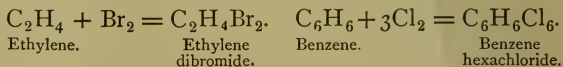
1. Hydrogen is removed in the form of haloid acid and replaced by the halogen. In this way, 1, 2, 3 or  $n$  units of hydrogen may be removed and replaced by 1, 2, 3 or  $n$  units of halogen, with formation of 1, 2, 3 or  $n$  unit-weights of haloid acid; consequently to effect the replacement of  $n$  units of hydrogen,  $2n$  units of chlorine or bromine are requisite. The number of units of hydrogen replaced depends mainly on the nature of the body operated upon, and on the temperature, but often other conditions also intervene. The following examples will serve to illustrate the mode of action :



2. Hydrogen is simply removed in the form of haloid acid, without replacement by the equivalent quantity of chlorine or bromine ; thus :

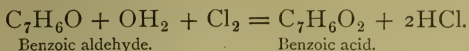


3. Certain 'unsaturated' compounds unite directly with chlorine or bromine ; for example :



4. Under ordinary conditions, chlorine and bromine only decompose water very slowly, setting free oxygen ( $\text{OH}_2 + \text{Cl}_2 = \text{O} + 2\text{HCl}$ ), but in the presence of a third body possessing a tendency to combine with oxygen this decomposition occurs far more readily ; hence in many cases chlorine and bromine in presence of water act as powerful oxidising agents ;<sup>1</sup> e.g. :

<sup>1</sup> A class of reactions analogous to this is often met with in the study of the so-called inorganic compounds. Thus chlorine is without

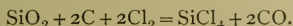


A point of great interest with regard to the action of chlorine, especially on organic bodies, is the influence of light on the course of the reaction. We know that chlorine and hydrogen do not combine in the dark, and only slowly in diffused light, but that they unite immediately under the influence of a bright light. Similarly chlorine is entirely without action on benzene in the dark, or even in diffused light, whilst direct union occurs readily when a mixture of these bodies is exposed to bright sunlight ( $\text{C}_6\text{H}_6 + 3\text{Cl}_2 = \text{C}_6\text{H}_6\text{Cl}_6$ ). More remarkable still, if *monochloropropylene*,  $\text{C}_3\text{H}_5\text{Cl}$ , be acted upon by chlorine in the dark, it is converted into the substitution derivative *dichloropropylene* ( $\text{C}_3\text{H}_5\text{Cl} + \text{Cl}_2 = \text{C}_3\text{H}_4\text{Cl}_2 + \text{HCl}$ ), but in bright sunlight under otherwise similar conditions the additive<sup>1</sup> compound,  $\text{C}_3\text{H}_5\text{Cl}_3$ , is formed ( $\text{C}_3\text{H}_5\text{Cl} + \text{Cl}_2 = \text{C}_3\text{H}_5\text{Cl}_3$ ).

Bromine exhibits, though in a less marked degree, a similar behaviour: combining directly with benzene to form the additive compound,  $\text{C}_6\text{H}_6\text{Br}_6$ , in bright sunlight, but yielding substitution derivatives, such as  $\text{C}_6\text{H}_5\text{Br}$ ,  $\text{C}_6\text{H}_4\text{Br}_2$ , &c., when the action is carried on in diffused light.

A further point of interest is the simultaneous formation of isomeric products by the action of chlorine. Thus, on treating

action on silicic anhydride at a red heat, but in presence of carbon it readily converts it into silicic tetrachloride:



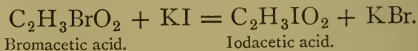
In this case the tendency of the carbon to unite with the oxygen, added to the tendency of the chlorine to unite with the silicium, is sufficient to overcome the tendency of the silicium to remain combined with the oxygen, which the chlorine alone is not able to overcome.

<sup>1</sup> Compounds formed by the replacement of one element by the equivalent quantity of another element are termed 'substitution' derivatives, and compounds formed by the direct union of two bodies are often termed 'additive' compounds.

$\beta$ -chloropropane (*isopropyl chloride*),  $C_3H_7Cl$ , with chlorine, a mixture of two bodies, each of the composition  $C_3H_6Cl_2$ , is obtained ; one of these boils at  $70^\circ$ , the other at  $96^\circ$ , and they differ also in many other respects. Several similar cases might be quoted.

Iodine combines directly with certain unsaturated compounds, ethylene for example ( $C_2H_4 + I_2 = C_2H_4I_2$ ), and sometimes also in presence of water acts as an oxidising agent, but both classes of reaction are effected far less readily than by bromine or chlorine. Iodo-substitution derivatives are never formed by the direct action of iodine on hydrogenised compounds, unless the hydriodic acid produced be immediately withdrawn from the sphere of action. To effect this, mercuric oxide, or iodic acid, is simultaneously added, which reacts with the haloid acid to form, in the one case, mercuric iodide and water ( $HgO + 2HI = HgI_2 + OH_2$ ), in the other free iodine and water ( $HIO_3 + 5HI = 3I_2 + 3OH_2$ ). To prepare iodophenol, for example, from phenol, we add iodine and the requisite quantity of mercuric oxide to an alcoholic solution of phenol: iodophenol and hydriodic acid are formed ( $C_6H_6O + I_2 = C_6H_5IO + HI$ ), but the latter immediately enters into reaction with the mercuric oxide and is converted into insoluble mercuric iodide.

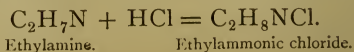
Iodo-substitution derivatives are often obtained from the corresponding chlorinated or brominated compounds, by double decomposition with potassic iodide ; e.g. :



*Action of Hydrochloric, Hydrobromic, and Hydriodic Acids.*

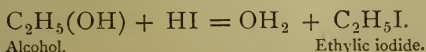
A variety of modes of action are to be distinguished.

1. These acids unite readily and at once in the cold with basic compounds such as the so-called 'compound ammonias,' the alkaloids, &c., forming salts ; e.g. :



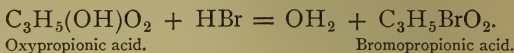
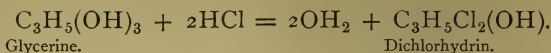
2. They combine with many 'unsaturated' compounds ; thus ethylene and hydriodic acid form monoiodoethane,  $\text{HI} + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_5\text{I}$  ; fumaric acid and hydrobromic acid form bromosuccinic acid,  $\text{C}_4\text{H}_4\text{O}_4 + \text{HBr} = \text{C}_4\text{H}_5\text{BrO}_4$ . In such cases it is usually necessary to heat the mixture during a shorter or longer period, and if the combination occur in the cold, a considerable time is required to render it complete ; hydriodic acid lends itself far more readily to reactions of this class than either hydrobromic or hydrochloric acid, and hydrobromic more readily than hydrochloric acid. The nature of the products depends very much on the conditions of experiment, on the temperature to which the mixture is heated, and the degree of concentration of the aqueous solution of haloid acid, and isomeric compounds are often obtained. Thus hydrobromic acid, by its action on *bromethylene*,  $\text{C}_2\text{H}_3\text{Br}$ , produces under one set of conditions *ethylene dibromide*,  $\text{C}_2\text{H}_4\text{Br}_2$ , which boils at  $129^\circ$  ; under other conditions an isomeric body boiling at  $110^\circ$ . Similarly, *bromopropylene*,  $\text{C}_3\text{H}_5\text{Br}$ , yields either *propylene dibromide*,  $\text{C}_3\text{H}_6\text{Br}_2$  (B.P.  $140^\circ$ – $143^\circ$ ), or the iso-meric compound boiling at  $122^\circ$ . Often, and indeed usually, a mixture of the isomeric compounds is produced, since it is difficult precisely to maintain the exact conditions necessary to the formation of the one or the other alone. The compounds with high boiling-points are principally formed at the ordinary temperature by the action of a very concentrated hydrobromic acid solution ; the isomeric bodies by the action of a less concentrated solution at a temperature of  $100^\circ$ .

3. Certain bodies exchange  $(\text{OH})'$ , *hydroxyl*, for chlorine, bromine, or iodine, when acted upon by the haloid acids. This mode of action is peculiarly characteristic of the so-called 'alcohols' and 'oxyacids.' The following examples may serve in illustration :—

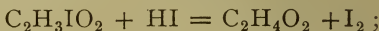


Alcohol.

Ethylic iodide.



The majority of iodine substitution compounds, however, are at once decomposed in contact with hydriodic acid, with separation of iodine and replacement of the iodine by the equivalent amount of hydrogen ; thus :

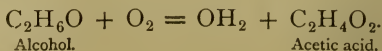


so that by acting upon oxypropionic acid, for example, with hydriodic acid, we obtain, not iodopropionic, but propionic acid ; the former is doubtless produced in the first instance ( $\text{C}_3\text{H}_5(\text{OH})\text{O}_2 + \text{HI} = \text{OH}_2 + \text{C}_3\text{H}_5\text{IO}_2$ ), it has but an ephemeral existence, however, being at once converted by the remaining hydriodic acid into propionic acid and iodine ( $\text{C}_3\text{H}_5\text{IO}_2 + \text{HI} = \text{C}_3\text{H}_6\text{O}_2 + \text{I}_2$ ).

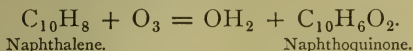
This peculiar behaviour of iodo-derivatives towards hydriodic acid at once gives a clue to the non-formation of iodo-substitution derivatives, by the action of iodine, in those cases in which the hydriodic acid first formed by the action of the iodine on the hydrogenised compound is not at once removed from the sphere of action.

In virtue of this property, possessed by hydriodic acid to so marked an extent, of removing oxygen from bodies and replacing it by hydrogen, it is one of the most powerful reducing agents known ; in fact, by the action of a very concentrated solution at high temperatures, most oxygenated compounds may ultimately be converted into the corresponding hydrogenised substances : thus acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , for example, is converted into ethane,  $\text{C}_2\text{H}_6$ , &c.

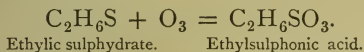
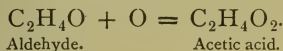
*Action of Oxidising Agents.*—1. Hydrogen is eliminated in the form of water and replaced by an *equivalent* quantity of oxygen ; thus :



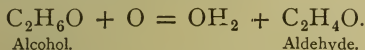
2. Hydrogen is eliminated in the form of water and replaced by *twice the equivalent quantity* of oxygen, as in the formation of the quinones, e.g. :



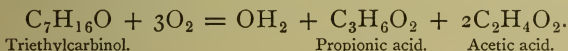
3. Oxygen is simply added on to the compound :



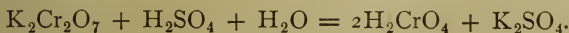
4. Hydrogen is simply eliminated :



5. The compound acted upon is split up and yields two or more *oxidised* bodies, each containing fewer units of carbon in its formula than the original substance, e.g. :

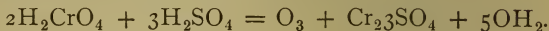


These reactions are the results of 'moderated' oxidation, and are obtained by employing, at most, a slight excess of the oxidising agent ; by a large excess, assisted by a high temperature, the majority of carbon compounds are ultimately resolved more or less readily into carbonic anhydride and water, just as by combustion with oxygen. Although in all the above cases the reactions are represented as occasioned by free oxygen, yet, as a matter of fact, they are seldom realised by employing free oxygen, but usually by evolving the oxygen in the immediate presence of the body to be acted upon, or, as it is termed, by *nascent* oxygen. The reagent most commonly employed is a mixture of potassic dichromate and sulphuric acid in aqueous solution, which enter into reaction according to the equation :





The chromic acid so produced, if in presence of a body possessing a tendency to take up oxygen, and an excess of sulphuric acid, readily parts with a portion of its oxygen, yielding chromic sulphate and water :

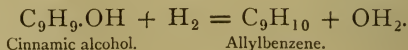


*Action of 'nascent' Hydrogen.*—We scarcely know an instance in which *free* hydrogen is able to act upon carbon compounds ; in the nascent state, however, i.e. at the moment of liberation from a state of combination, it is one of the most active and useful agents at the chemist's disposal. It is usual to add the compound, which it is desired to submit to the action of hydrogen, to a mixture of substances evolving hydrogen, such as sodium amalgam and water, zinc and sulphuric acid, or tin and hydrochloric acid. Hydriodic acid, sulphurous acid, and hydric sulphide, are also powerful reducing agents ; the first and last of these, although stable in the pure state, readily part with their hydrogen to bodies possessing a strong tendency to combine with, or take up hydrogen. Sulphurous acid acts by decomposing water and setting free the hydrogen, itself combining with the oxygen to form sulphuric acid ; this decomposition of water by sulphurous acid only takes place, however, in presence of a third body which has a strong tendency to take up hydrogen. The following are the modes of action of nascent hydrogen :—

1. It combines directly with certain unsaturated compounds ; e.g. :

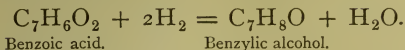
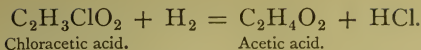


2. It removes oxygen without replacing it ; thus :

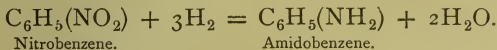


3. Oxygen, chlorine, bromine, or iodine are removed, but replaced by the equivalent quantity of hydrogen :



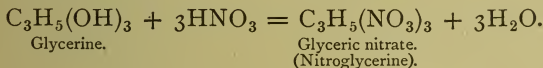
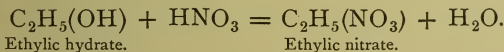


4. Oxygen is removed and replaced by half the equivalent quantity of hydrogen, in the reduction of *nitro-compounds* to *amido-compounds* :

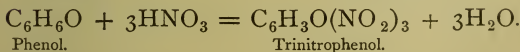
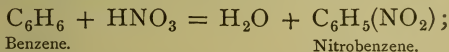


*Action of Nitric Acid.*—The concentrated acid acts most violently on many organic bodies, often completely destroying them, but the action may be moderated by the addition of water.

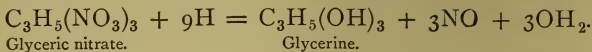
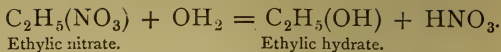
1. Nitric acid unites with basic substances forming salts.
2. It acts as an oxidising agent.
3. A 'nitric-ether,' or ethereal salt of nitric acid, is formed :



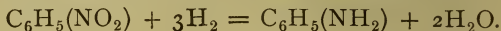
4. Nitro-substitution compounds are produced :



Apparently in cases 3 and 4 the two operations, if represented by empirical formulæ, are of the same order, and consist in the removal of  $n$  units of hydrogen from the compound in the form of water, and the addition of  $n$  times  $\text{NO}_2$ ; but the two classes of derivatives thus formed exhibit very dissimilar properties. The nitric ethers are readily decomposed by nascent hydrogen, and by heating them with water they are reconverted into their generators ; e.g :



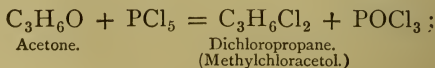
The nitro-compounds, on the other hand, are not affected by water or dilute alkaline solutions, but are readily reduced by nascent hydrogen and converted into amido-derivatives :



By the reduction of nitro-derivatives, therefore, products are obtained which still contain nitrogen, whilst the nitrogen is entirely removed from the nitric ethers by the action of reducing agents.

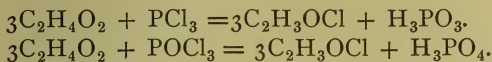
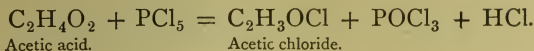
It is interesting to note, that experiment shows, that far less heat is evolved in the formation of the nitric ethers than in the formation of nitro-compounds, and to contrast this with the fact that the nitric ethers are, as a class, bodies of low stability, being readily decomposed by alkalies, and all highly explosive, whilst the majority of nitro-derivatives are far more stable substances and far less explosive. There is thus an evident relation between the amount of heat evolved and the nature of the product in the two cases, and we have a clear illustration of the circumstance that the less the amount of the chemical energy which is concerned in the production of a reaction between given substances, the less will be the amount of force necessary to cause the products of that reaction to exert the contrary action, and to re-form the parent substances, or otherwise to undergo alteration.

*Action of the haloid Phosphorus Compounds.*—1. These bodies either remove oxygen alone from the compound, replacing it by the equivalent quantity of halogen :



2. Or oxygen and hydrogen, one unit of halogen entering

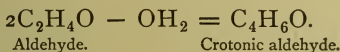
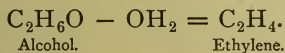
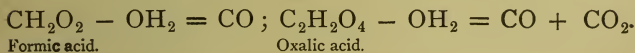
into the compound for every one unit of oxygen plus one of hydrogen removed ; thus :



3. In some instances phosphoric chloride ( $\text{PCl}_5$ ) behaves as a mixture of phosphorous chloride and chlorine ( $\text{PCl}_3 + \text{Cl}_2$ ), and simply chlorinates :

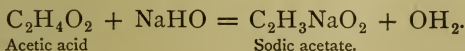


*Action of Dehydrating Agents.*—Phosphoric anhydride, hydric potassic sulphate, sulphuric acid, hydrochloric acid, zincic chloride, &c., when heated with many oxygenised bodies, cause the separation of the elements of water from them. Either the products contain:—1. Fewer units of carbon than the original compound ; 2, the same number of units ; 3, or a larger number. For example :



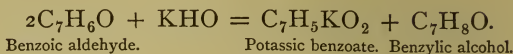
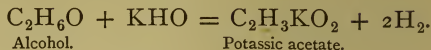
*Action of Alkalies.*—Potassic and sodic hydrates may act in a variety of ways :

1. With acids they form metallic salts by double decomposition :

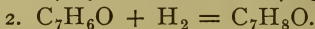
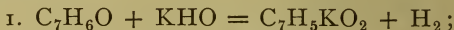


2. They act as oxydising agents, but at the same time

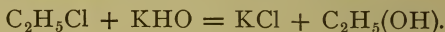
hydrogen is always evolved, so that in the end a mixed result is often obtained :



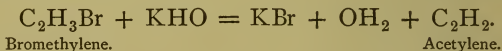
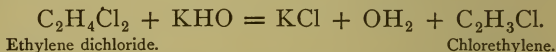
In the latter case two phases in the reaction are to be distinguished :



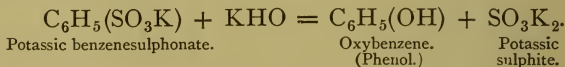
3. The action of the alkalies on chlorine, bromine, and iodine-substitution compounds leads in some cases to the replacement of the halogen by (OH) ; thus :



But more often the whole or part of the halogen is removed together with an equivalent quantity of hydrogen :



4. On fusion of the potassic or sodic salts of the sulpho-acids with potassic hydrate the corresponding oxy-derivatives are produced ; e.g. :



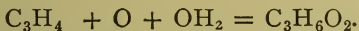
*Hydration of Organic Compounds.*—Under this heading is included a series of reactions which depend on the direct assumption of the elements of water by organic bodies ; this being sometimes, but by no means always, attended by the splitting up of the compound into simpler substances. An especial degree of interest attaches to them, inasmuch as they undoubtedly play a most important part in the pro-

cesses which occur in the economy of plants and animals. This direct assumption of water takes place in some cases spontaneously at ordinary temperatures ; in others more or less prolonged heating is requisite ; in others, again, the presence of third bodies assists the action to a remarkable extent. An instructive example of this mode of action is furnished by the conversion of cane sugar into a mixture of dextrose and lævulose ( $C_{12}H_{22}O_{11} + OH_2 = C_6H_{12}O_6 + C_6H_{12}O_6$ ), which takes place slowly when sugar is heated with water, and rapidly when a small proportion of hydrochloric, or sulphuric acid is added.

Hydration and oxidation very frequently occur simultaneously ; thus acetylene and oxygen in presence of water furnish acetic acid :



and similarly allylene, oxygen, and water yield propionic acid :



This form of action is doubtless also of very great importance in the operations of plant and animal life.

*Action of Heat.*—The majority of organic bodies are decomposed under the influence of heat. In many cases the reactions which occur are perfectly definite and simple, as, for example, in the decomposition of gallic acid by heat :



Gallic acid.

Pyrogallol.

But as a rule, especially if the temperature employed be at all elevated, a complex series of products are obtained having no simple relation to the parent compound. Heat tends both to simplify and to complicate organic bodies, but the more complex the body the more easily does it undergo decomposition as a rule : thus the higher hydrocarbons yield simpler products when their vapour is passed through a red-hot tube ; e.g. :

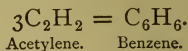


Naphthalene.

Benzene.

Acetylene.

but many simple hydrocarbons are converted into more complex bodies by heat ; e.g :



## CHAPTER IV.

### CARBON.

SINCE this element has already been treated of at considerable length in a previous volume of this series, only a few points there unnoticed need be here referred to.

The combustion of the several modifications of carbon with an excess of oxygen furnishes different amounts of heat. The figures in the following table represent the number of heat-units<sup>1</sup> disengaged on combustion of 12 grammes of each variety :

|                  |   |   |   |   |              |
|------------------|---|---|---|---|--------------|
| Diamond          | . | . | . | . | 93,240 units |
| Iron graphite    | . | . | . | . | 93,144 „     |
| Natural graphite | . | . | . | . | 93,564 „     |
| Gas carbon       | . | . | . | . | 96,564 „     |
| Wood charcoal    | . | . | . | . | 96,960 „     |

Corresponding differences are observed in their behaviour with reagents ; thus a mixture of potassic chlorate and concentrated nitric acid is entirely without action on diamond, even in the finest state of division ; by its action on the various sorts of graphite, *graphitic acid* is formed, whilst amorphous carbon is entirely dissolved by the mixture with formation of humus-like products.

*Graphitic Acid*.—The formula of this body, according to Brodie, is  $\text{C}_{11}\text{H}_4\text{O}_5$  ; according to Gottschalk,  $\text{C}_{33}\text{H}_{12}\text{O}_{18}$ . The product from natural graphite is obtained in yellow microscopic crystals of the rhombic or monoclinic system. When heated, it decomposes with explosion, incandescence, and evolution of

<sup>1</sup> The heat-unit here employed is the amount of heat necessary to raise the temperature of 1 gramme of water 1° C.



gas, leaving a finely-divided black residue, which still contains oxygen and hydrogen.

Carbon is slowly attacked by many oxidising agents, carbonic anhydride being always the main product. Thus chromic acid solution produces a small quantity of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ . Potassic permanganate has been found to yield traces of formic acid,  $\text{CH}_2\text{O}_2$ , and it is stated that by the action of this reagent under certain conditions, *Mellitic acid*,  $\text{C}_{12}\text{H}_6\text{O}_{12}$ , is obtained. Mellitic acid is the chief constituent of the so-called honey-stone which is found in the coal measures; hence its formation by the direct oxidation of carbon is of very great interest.

Pure amorphous carbon is not attacked when heated with a concentrated aqueous solution of hydriodic acid, but wood charcoal and coal are more or less acted upon and converted into hydrocarbons (paraffins).

The different forms of amorphous carbon ordinarily met with are more or less impure. Even the carbon obtained by heating pure organic substances, such as sugar, is not pure, but retains small quantities of hydrogen and oxygen; these may be removed by heating it intensely for some time in a current of dry chlorine. Pure amorphous carbon may also be prepared by heating potassium or sodium in carbonic anhydride.

*Carbonic Oxide* (Carbon monoxide, Carbonous oxide),  $\text{CO}$ .—The mode of preparation and main properties of this gas are already known to the student.

Carbonic oxide is decomposed by strongly-heated potassium or sodium with separation of carbon, but it is absorbed by potassium heated to about  $80^\circ$ , forming a highly explosive compound of the formula  $\text{C}_n\text{K}_n\text{O}_n$ .

The product thus obtained is decomposed with explosive violence by water, but may be preserved unchanged under dry petroleum oil. If exposed to moist air, it rapidly changes colour, and, it is said, then contains, according to the stage of decomposition, the potassium salt of one of the following acids:



*Trihydrocarboxylic acid*,  $C_{10}H_{10}O_{10}$ ; *Dihydrocarboxylic acid*,  $C_{10}O_{10}H_8$ ; *Hydrocarboxylic acid*,  $C_{10}O_{10}H_6$ ; or *Carboxylic acid*,  $C_{10}O_{10}H_4$ . By direct decomposition of the fresh mass with water, the potassium salt either of *Croconic acid*,  $C_5O_5H_2$ , or of *Rhodizonic acid*,  $C_5O_6H_4$ , or a mixture of the two, is obtained. All these compounds are extremely unstable.

Carbonic oxide combines directly with platinous chloride to form the following series of crystalline compounds :



On passing chlorine and carbonic oxide simultaneously over finely-divided metallic platinum, heated to about  $240^\circ$ , a mixture of  $C_2O_2PtCl_2$  and  $C_3O_3Pt_2Cl_4$  is obtained, which may be separated by boiling the mass with carbonic tetrachloride; this dissolves, chiefly the latter, leaving a residue consisting of the compound  $C_2O_2PtCl_2$ . Either of these bodies splits up, when heated, into carbonic oxide and the compound  $COPtCl_2$ ; conversely, the latter yields a mixture of  $C_2O_2PtCl_2$  and  $C_3O_3Pt_2Cl_4$  when heated in an atmosphere of carbonic oxide. Water decomposes these substances; thus :



*Carbonic Oxychloride* (Carbonyl chloride; Phosgene; Chlorocarbonic acid),  $COCl_2$ .—Carbonic oxide and chlorine do not unite in the dark, but combine readily when the mixture is exposed to bright light (sunlight). Combination also ensues on passing the mixed gases over heated platinum-black, or into boiling antimonious pentachloride. Carbonic oxychloride may also be obtained by the action of sulphuric anhydride on carbonic tetrachloride :



It is a colourless gas possessing an extremely suffocating, tear-exciting odour. It may be condensed, by passing it through a U tube surrounded by a mixture of ice and salt, to a colourless, mobile liquid boiling constantly at  $8.2^\circ$ . It is immediately decomposed by water.

*Carbonic Anhydride* (Carbon dioxide; carbonic acid),  $CO_2$ .—The union of carbon and oxygen is accompanied by

the evolution of much heat ; but it is a noteworthy circumstance that far less is evolved in the conversion of carbon into carbonic oxide, than in the conversion of the latter into carbonic anhydride. Thus the union of 12 grammes of carbon with 16 grammes of oxygen gives rise to the disengagement of about 25,000 heat-units, but the conversion of these  $12 + 16 = 28$  grammes of carbonic oxide into carbonic anhydride, that is to say, the fixation of a further 16 grammes of oxygen by the 12 grammes of carbon, is attended by the evolution of no less than 69,000 heat-units.

The probable explanation of this remarkable difference is, that heat is absorbed in converting the solid carbon into gaseous carbon, in which latter condition it doubtless exists in carbonic oxide and anhydride. This view is supported by the fact that sensibly equal quantities of heat are evolved in the fixation of each successive 16 grammes of oxygen in the formation of the two oxides of tin, of copper, and of phosphorus, in all of which cases the products are solid. Thus, the oxidation of tin to stannous oxide (Sn to SnO) is accompanied by the disengagement of 34,900 heat-units, and to stannic oxide (Sn to SnO<sub>2</sub>) by the disengagement of 68,900 units, or about double ; in the formation of cuprous oxide, the union of  $63 \times 2$  grammes of copper with 16 grammes of oxygen (Cu<sub>2</sub> to Cu<sub>2</sub>O) evolves 18,000 units, whilst the combination of 63 grammes of copper with 16 grammes of oxygen, to form cupric oxide (Cu to CuO), furnishes 38,000 units.

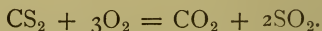
*Carbonic Disulphide* (Carbonic sulphanhydride ; Bisulphide of carbon) CS<sub>2</sub>.—Carbon and sulphur do not combine when simply heated together in the solid state, owing to the volatilisation of the sulphur at a temperature below that at which combustion can take place ; their union may be readily effected, however, by passing sulphur vapour over red-hot carbon.

It is noteworthy that the formation of carbonic disulphide is attended by an *absorption* of heat ; this will be evident from the following comparison of its heat of combustion with the heats of combustion of its constituents :—

|                           |         |
|---------------------------|---------|
| C . . . . .               | 94,000  |
| S <sub>2</sub> . . . . .  | 142,000 |
|                           | <hr/>   |
|                           | 236,000 |
| CS <sub>2</sub> . . . . . | 258,000 |
|                           | <hr/>   |
|                           | -22,000 |
|                           | <hr/>   |

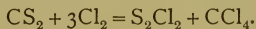
The union of 64 grammes of sulphur with 12 grammes of carbon thus requires the absorption of no less than 22,000 heat-units, and this fact explains how it is that in order to combine carbon with sulphur it is necessary to apply heat throughout the whole course of the operation, whereas the combustion of carbon in oxygen, when once commenced, proceeds spontaneously, owing to the large amount of heat evolved in the process.

Pure carbonic disulphide is a mobile, colourless, strongly-refracting liquid, almost insoluble in water, possessing a faint unpleasant odour, of sp. gr. 1.29 at 0°. It boils at 46°, and is extremely volatile and inflammable; its vapour when mixed with air is highly explosive :



It dissolves sulphur, phosphorus, iodine, oils, &c., and is largely used in the arts and manufactures on account of its solvent power.

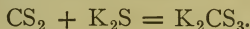
*Action of Chlorine on CS<sub>2</sub>.*—The ultimate product of the action of dry chlorine in presence of iodine or antimonie pentachloride is carbonic tetrachloride :



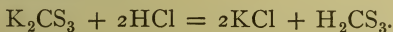
Two intermediate products of the composition,  $\text{CSCl}_4$  (*perchloromethyl mercaptan*) and  $\text{C}_2\text{S}_3\text{Cl}_6$ , may be isolated if the action of chlorine in presence of iodine be not carried too far; the latter is a magnificently crystalline body, the former an oily liquid. Moist chlorine exercises simultaneously both a chlorinating and an oxidising action, and gives rise to the following products:  $\text{CSCl}_2$ , *sulphocarbonyl chloride*;  $\text{CSCl}_4$ , *perchlormethyl mer-*

*captan* ; and  $\text{CSCl}_4\text{O}_2$ , *trichlormethyl sulphurous chloride*. By the prolonged action of bromine and antimonie pentabromide on  $\text{CS}_2$  at high temperatures, carbonic tetrabromide,  $\text{CBr}_4$ , is formed.

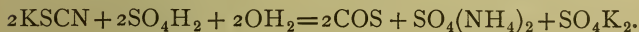
Carbonic disulphide enters into combination with the metallic sulphides to form *sulphocarbonates*, in exactly the same way that carbonic anhydride unites with the metallic oxides, forming metallic carbonates :



Sulphocarbonic acid is readily obtained as a yellow, easily decomposable oily liquid on treating a sulphocarbonate with dilute hydrochloric acid :



*Carbonic Oxysulphide*,  $\text{COS}$ , is obtained by the action of moderately dilute sulphuric acid on potassic sulphocyanate :



Also on gently heating a mixture of carbonic disulphide and sulphuric anhydride :

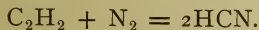


It is a colourless gas, easily decomposed by heat into carbonic oxide and sulphur, possessing a faint, not unpleasant, odour. It is completely absorbed, though less rapidly than carbonic anhydride, by potassic hydrate solution, and is at the same time decomposed :



#### CYANOGEN COMPOUNDS.

*Hydrocyanic Acid*,  $\text{HCN}$ .—The most direct synthesis of this compound is effected by passing electric sparks through a mixture of acetylene and nitrogen gases :



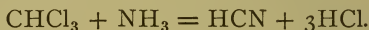
It is not necessary, in order to realise this synthesis, to prepare pure acetylene, but the experiment may be shown by passing the electric sparks through nitrogen saturated with ben-

zene vapour : the latter is partially decomposed into acetylene ( $C_6H_6 = 3C_2H_2$ ), which then enters into union with the nitrogen. A current of nitrogen is therefore transmitted first through a flask containing benzene and then into a glass globe provided with platinum wire poles, between which electric sparks are constantly passing ; the issuing gas is washed by water, which dissolves the hydrocyanic acid, and the latter may afterwards be shown to be present by the application of the ordinary characteristic tests to the solution.

Hydrocyanic acid is also formed : 1. By the action of heat on ammoniac formate :



2. By the action of ammonia on chloroform, the reaction being greatly facilitated by the addition of a small quantity of an alcoholic solution of potassic hydrate :



3. By the action of acids on metallic cyanides :

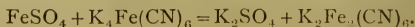


The anhydrous acid is prepared by decomposing argentic or mercuric cyanide by dry gaseous hydrochloric acid, or hydric sulphide. It is a colourless liquid of scarcely acid reaction, which boils at  $26.5^\circ$  and solidifies at  $-15^\circ$ . Specific gravity  $.705$  at  $7^\circ$ . It is soluble in water and alcohol in all proportions ; both the anhydrous and strong aqueous acid are inflammable, and possess an odour resembling that of bitter almonds. It is a *most violent poison*, so that the greatest caution must be exercised when dealing with it.

An aqueous solution of the acid is most conveniently obtained by distilling potassic ferrocyanide with dilute sulphuric acid :

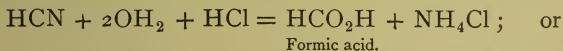


<sup>1</sup> This product is identical with the precipitate which is produced on adding a ferrous salt to a solution of potassic ferrocyanide :—

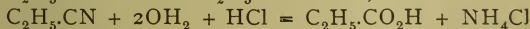
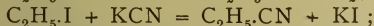


If a concentrated acid be required, a mixture of 10 parts coarsely-powdered ferrocyanide, 6 parts ordinary sulphuric acid, and 14 parts of water is employed ; if a weaker acid, 30-40 parts of water are added. The mixture is placed in a flask connected with a condenser and receiver, the latter being provided with a tube to carry any uncondensed vapour away from the operator into the open air, or chimney of the laboratory. The flask is carefully heated on a sand bath and shaken from time to time, otherwise the contents of the flask are liable to bump violently and endanger its breaking.

The pure acid is very unstable, decomposing spontaneously with formation of a brown amorphous product and ammonia. The aqueous acid behaves similarly, ammoniac formate being one of its decomposition-products. The presence of a trace of a mineral acid, however, increases the stability of the aqueous acid in a remarkable manner, although if the solution be heated with a mineral acid, or an alkali, it is rapidly decomposed according to the equation :



These reactions, by which the conversion of the (CN) group into the (CO<sub>2</sub>H = CO.OH) group is effected, are of great importance, as they afford a general method of synthesising acids, and of converting acids of lower into acids of higher basicity ; for example, ordinary alcohol may be converted into propionic acid by the following series of reactions :

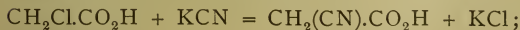


Similarly, monobasic acetic is transformed into dibasic malonic acid .



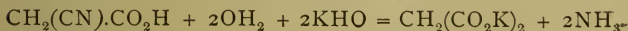
Acetic acid.

Chlo. acetic acid.



Chloroacetic acid.

Cyanoacetic acid.



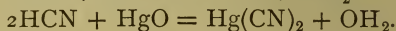
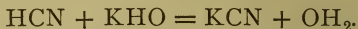
Cyanoacetic acid.

Potassic malonate.



Hydrocyanic acid unites directly with hydrochloric, hydrobromic, and hydriodic acids, forming white, crystalline, easily decomposable compounds:  $\text{HCN} + \text{HCl} = \text{CH}_2\text{NCl}$ .

*Metallic cyanides* are formed by the action of the metallic oxides and hydrates on hydrocyanic acid :



Potassic cyanide is also formed on passing nitrogen over a mixture of potassic carbonate and carbon heated to redness :



It is often found in the iron blast-furnaces, formed in virtue of this reaction from the potassic salts present in the materials smelted, and the carbon and nitrogen in the fuel.

*Detection and Estimation of Hydrocyanic Acid.*—The solution suspected to contain hydrocyanic acid is rendered alkaline by potassic hydrate, small quantities of ferrous sulphate and ferric chloride solutions are then added, and finally, sufficient hydrochloric acid to redissolve the precipitated ferrous and ferric hydrates. If a dark blue precipitate remain, or if the solution be of a green colour and deposit a blue precipitate on standing, it is evidence of the presence of hydrocyanic acid or a cyanide in the solution tested. The explanation of this test is as follows : supposing the solution to have contained free hydrocyanic acid, on the addition of potassic hydrate this becomes potassic cyanide, which reacts on the ferrous salt subsequently added to form potassic ferrocyanide :



The blue precipitate is produced by the action of the ferric salt on the ferrocyanide :

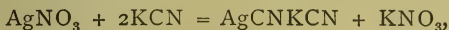


and the hydrochloric acid is added to dissolve the ferrous and ferric hydrates precipitated by the excess of potassic hydrate.

The quantitative determination of hydrocyanic acid depends on the fact that potassic and argentic cyanides unite to form a

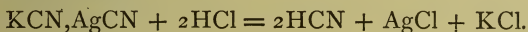


soluble double cyanide,  $\text{KCN}, \text{AgCN}$  : the hydrocyanic acid is therefore first converted into potassic cyanide by the addition of potassic hydrate, a solution of argentic nitrate of *known strength* is then dropped in, until the precipitate which first forms no longer disappears on shaking ; at this point the whole of the cyanide is converted into the double salt, consequently, the amount of silver solution added being known, it is easy to calculate the amount of hydrocyanic acid present from the equation :

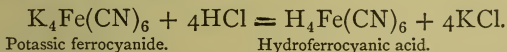


which tells us that every 170 parts of argentic nitrate correspond to 130 parts of potassic cyanide, or 54 parts of hydrocyanic acid.

*Double Cyanides.*—A large number of metallic cyanides combine with each other to form so-called double cyanides. Most of these when acted upon by mineral acids evolve hydrocyanic acid and produce the corresponding salts of both metals, thus :



The double cyanides of iron, cobalt, and chromium, however, behave differently : when treated with acids no hydrocyanic acid is evolved, and only one of the metals is replaced by hydrogen, thus :

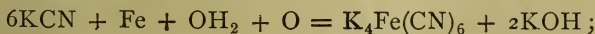


Potassic ferrocyanide.

Hydroferrocyanic acid.

Hydroferrocyanic acid thus prepared is a white crystalline powder which rapidly becomes blue on exposure to the air. It is a strong acid, decomposing carbonates and acetates readily.

Pure cyanides of iron have never yet been obtained, so great is the tendency on the part of iron to form double cyanides. Even metallic iron is dissolved by potassic cyanide : if the air have access, the reaction takes place as represented by the equation :



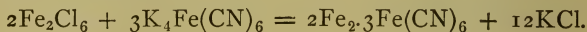
but if oxygen be carefully excluded, hydrogen is evolved :



Potassic ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ , is prepared on the large scale by fusing dry refuse animal matter, such as horn-parings, leather scraps, &c., with crude potassic carbonate and iron filings or turnings in large iron vessels. The cooled mass is subsequently exhausted with hot water, the solution is evaporated to crystallisation, and the crude salt thus obtained purified by recrystallisation. A number of reactions occur during this process : in the first place, potassic cyanide is formed by the union of the potassium of the potassic carbonate with the nitrogen and carbon of the animal matters ; on subsequent treatment of the fused mass with water, the potassic cyanide is dissolved, but immediately reacts on the metallic iron and ferrous sulphide<sup>1</sup> to form potassic ferrocyanide. The ferrous sulphide is derived partly from the sulphur in the animal matter, and partly from the potassic sulphate present in the crude carbonate.

The pure salt crystallises in large, pale yellow tetragonal pyramids of the composition  $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{OH}_2$  ; it is readily soluble in water, and is not poisonous.

Potassic ferrocyanide (yellow prussiate of potash) is largely employed in the manufacture of prussian blue for dyeing purposes ; this is formed by mixing solutions of potassic ferrocyanide and ferric chloride, and is, in fact, ferric ferrocyanide :

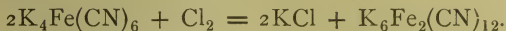


At a red heat potassic ferrocyanide is decomposed into potassic cyanide, nitrogen, and so-called carbide of iron.

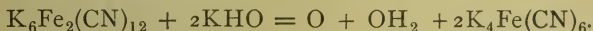
*Potassic Ferricyanide.*—By the action of oxidising agents on potassic ferrocyanide, this salt loses a portion of its potassium and is converted into potassic ferricyanide. The latter is usually prepared by the action of chlorine either on the dry salt, or on an aqueous solution, the con-

<sup>1</sup>  $\text{FeS} + 6\text{KCN} = \text{K}_2\text{S} + \text{K}_4\text{Fe}(\text{CN})_6.$

version of the ferrocyanide being complete when on the addition of ferric chloride a blue precipitate is no longer produced :



Potassic ferricyanide (red prussiate of potash) forms large ruby-red prismatic crystals, readily soluble in water. In the presence of compounds capable of undergoing oxidation (i.e. of giving up hydrogen, or of taking up oxygen), and in alkaline solution, it acts as a powerful oxidising agent, being reconverted into ferrocyanide :



Soluble ferricyanides yield a dark blue precipitate<sup>1</sup> of ferrous ferricyanide (Turnbull's blue) with ferrous salts ; a brown coloration with ferric salts.

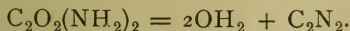
*Cyanogen*,  $C_2N_2 = (CN)_2$ .—Cyanogen cannot be formed, except perhaps in very minute quantities, by direct union of its elements. The combination of carbon and nitrogen to form cyanogen would, it is ascertained, be attended by the absorption of a large amount of heat.

It may be obtained :

1. By the decomposition of the cyanides of mercury, silver, and gold by heat :— $Hg(CN)_2 = C_2N_2 + Hg$ .

A certain quantity of a brown amorphous substance (so-called *paracyanogen*), having the same composition as cyanogen, and which is doubtless a polymeric modification, is always produced simultaneously. This paracyanogen is completely converted into gaseous cyanogen by heating to  $860^\circ$ .

2. By the dry distillation of *oxamide*,  $C_2O_2(NH_2)_2$ , or ammonic oxalate,  $C_2O_4(NH_4)_2$  :



Cyanogen is a colourless, extremely poisonous gas, possessing a characteristic odour resembling that of bitter

<sup>1</sup>  $K_6Fe_2(CN)_{12} + 3FeSO_4 = 3K_2SO_4 + (Fe_3)Fe_2(CN)_{12}.$

almonds. It is readily condensed by the application of pressure, or cold, to a mobile liquid, which solidifies a few degrees below  $-30^{\circ}$  to a crystalline solid. It burns in oxygen or air with a violet flame.

In its chemical behaviour cyanogen exhibits the closest relations to the monad elements chlorine, bromine, and iodine, entering into combination with, and replacing, monad elements, and forming derivatives which in many respects closely resemble those yielded by these elements under similar conditions. For example, the action of cyanogen on a solution of potassic hydrate, which yields a mixture of potassic cyanide and cyanate :

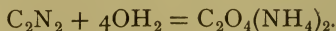


is the precise analogue of that which occurs when chlorine acts upon potassic hydrate :



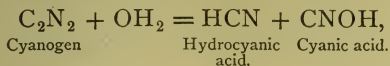
It was the discovery of this peculiar property of this body which first gave rise to the assumption of compound organic radicles,<sup>1</sup> or groups of elements capable of being transferred unaltered from compound to compound: the molecule of cyanogen being assumed to contain twice the monad compound radicle ( $\text{C}^{\text{iv}}\text{N}'''$ ), just as the molecules of hydrogen, of chlorine, &c., are assumed to be constituted as represented by the formulæ  $\text{H}_2$ ,  $\text{Cl}_2$ .

Both aqueous and alcoholic solutions of cyanogen decompose spontaneously, depositing a brown powder (azulmic acid). The main product of decomposition in aqueous solution is ammonic oxalate :

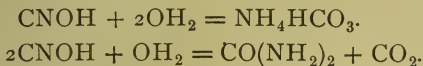


<sup>1</sup> An element is regarded as a simple radicle, and in the same way that we speak of monad, dyad, or triad elements so we speak of monad, dyad, or triad compound radicles, meaning thereby that these are equivalent in combining or replacing power to one, two, or three unit-weights of hydrogen.

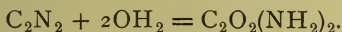
At the same time, however, small quantities of ammoniac carbonate, hydrocyanic acid, and urea are produced, thus :



but the cyanic acid in presence of water is at once converted partly into hydric ammoniac carbonate, partly into urea,  $\text{CO}(\text{NH}_2)_2$

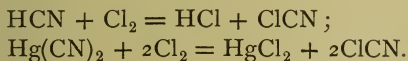


The presence of aldehyde, or of hydrochloric acid, in the aqueous solution has a remarkable effect in retarding the assimilation of water ; in this case. oxamide is produced in place of ammoniac oxalate :



Cyanogen is similarly, although more rapidly converted into oxalic acid by digestion with a solution of potassic hydrate, or of a mineral acid.

*Chlorides of Cyanogen.*—By the action of chlorine on hydrocyanic acid, or on metallic cyanides, the hydrogen or metal is replaced by chlorine, and a chloride of cyanogen is produced, thus :



Three such compounds have been described : one is gaseous ; the second is a liquid boiling at  $12.6^\circ$  ; the third is a crystalline solid boiling at  $190^\circ$ . It is probable, however, that the gaseous chloride is simply the vapour of the liquid chloride.

Liquid cyanogen chloride ( $\text{CNCl}$ ) is obtained by passing chlorine into a solution of 1 part of hydrocyanic acid in 5 parts of water cooled by a mixture of ice and salt until the liquid assumes a green colour ; it separates as an oily layer at the bottom of the liquid mass.

Solid cyanogen chloride ( $C_3N_3Cl_3$ ), which is polymeric with the liquid chloride, is prepared by passing chlorine into a well-cooled solution of 1 part hydrocyanic acid in 4 parts anhydrous ether, and separates in the crystalline form after some time.

Similarly, two bromides of cyanogen of the composition represented by the formulæ  $CNBr$  and  $C_3N_3Br_3$  respectively, and a crystalline iodide,  $CNI$ , are known.

*Hydrates of Cyanogen.*—These may be regarded as derived from the above chlorides by the replacement of chlorine by hydroxyl ( $OH$ ). The following are known :—

*Cyanic acid*,  $CNOH$  ; *Cyanuric acid*,  $C_3N_3O_3H_3$  ; and *Cyamelide*,  $n(CNOH)$ , a compound of the same percentage composition as these, the unit-weight of which is yet unknown.

The compound intermediate between the first and second of the above, *Dicyanic acid*,  $C_2N_2O_2H_2$ , does not appear to have been obtained in a pure state.

These bodies are chiefly interesting on account of the remarkable manner in which they pass from one condition to the other : thus if acetic acid be added to a cyanate in insufficient quantity to decompose it entirely, it is converted into cyanurate ; cyanuric acid is converted by heat into cyanic acid, which changes spontaneously into cyamelide ; cyamelide is converted by heat into cyanic acid, and by the action of alkalis into cyanuric acid. Another of the most interesting changes occurring in this series is the spontaneous conversion of ammoniac cyanate,  $CNO(NH_4)$ , into *urea*,  $CO(NH_2)_2$ , the amide of carbonic acid.

*Cyanic Acid*,  $CNOH$ .—The sole method of preparation is by distillation of dry cyanuric acid. Cyanates are readily obtained by the direct oxidation of cyanides : thus potassic cyanide is converted into potassic cyanate, by fusion with manganic peroxide, or plumbic oxide :

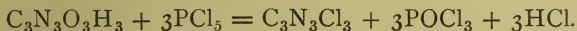




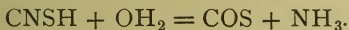
The formation of potassic cyanate by the action of cyanogen on a solution of potassic hydrate has been previously described.

Cyanic acid cannot be prepared by the double decomposition of cyanates by acids, since it is rapidly converted in presence of water into ammonic carbonate and urea. Pure cyanic acid is a colourless, strongly acid liquid, of extremely pungent odour; at  $0^{\circ}$  C. it changes spontaneously in an hour into white crystalline cyamelide.

*Cyanuric Acid*,  $C_3N_3O_3H_3$ , is obtained by the action of heat, or of chlorine, on urea; also by double decomposition of solid cyanogen chloride by water. It is only completely converted into ammonic carbonate after long-continued boiling with water. It yields solid cyanogen chloride when submitted to the action of phosphorus pentachloride:



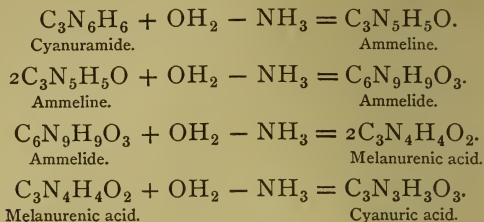
*Sulphocyanic Acid*, CNSH.—The most important salt of this acid, potassic sulphocyanate, is readily formed by heating a mixture of potassic cyanide and sulphur in equivalent proportions for some time to fusion. Potassic sulphocyanate crystallises in long white, highly deliquescent prismatic needles. Sulphocyanic acid, like cyanic acid, is extremely unstable, and is readily converted in presence of water into carbonic oxysulphide (p. 59) and ammonia:



*Cyanamide*,  $CN(H_2N)$ , is obtained by the action of gaseous chloride of cyanogen on ammonia. It is a white crystalline body, which melts at  $40^{\circ}$ . If an aqueous solution of it be left to itself for some time, it deposits a sparingly soluble crystalline substance, which is probably *dicyanamide*,  $C_2N_4H_4$ . When heated to  $150^{\circ}$ , cyanamide solidifies with considerable evolution of heat, and is converted into *cyanuramide* or *melamine*,  $C_3N_6H_6$ . By the action of strong acids (sulphuric acid) cyanuramide is finally converted into cyanuric acid, but a series of intermediate



products are obtained, each derived from the preceding by the addition of  $\text{OH}_2$  and elimination of  $\text{NH}_3$  :—



## CHAPTER V.

### HYDROCARBONS.

#### $\text{C}_n\text{H}_{2n+2}$ OR MARSH GAS SERIES. PARAFFINS.

THE name 'paraffin'<sup>1</sup> has long been applied to a mixture of the solid hydrocarbons of this series, and many of the liquid members are known commercially as 'paraffin oils'; hence it has been proposed by Mr. Watts to employ it as a generic term indicating the chemical indifference which, indeed, is especially characteristic of the entire group now under consideration.

A large number of these paraffins are known; they constitute, in fact, a complete *homologous* series, each term of which, from  $\text{CH}_4$ , the first member, upwards differs from the term next below in the series by  $\text{CH}_2$ . The first three members of the series are gaseous; those following are liquid, but become more and more viscid and less volatile as the series is ascended; whilst the highest terms are crystalline solids. There is also a gradual increase in specific gravity from term to term. These gradual alterations in physical properties are attended by slight alterations in chemical

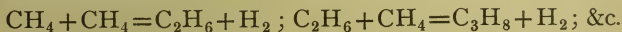
<sup>1</sup> From *parum*, *affinis*.

behaviour, although the members exhibit the same general behaviour throughout the entire series.

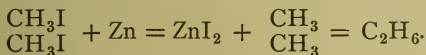
The following are the names and formulæ of the first ten members of the series :—

|        |               |                                |               |                                 |
|--------|---------------|--------------------------------|---------------|---------------------------------|
| Butane | Methane . . . | CH <sub>4</sub>                | Hexane . . .  | C <sub>6</sub> H <sub>14</sub>  |
|        | Ethane . . .  | C <sub>2</sub> H <sub>6</sub>  | Heptane . . . | C <sub>7</sub> H <sub>16</sub>  |
|        | Propane . . . | C <sub>3</sub> H <sub>8</sub>  | Octane . . .  | C <sub>8</sub> H <sub>18</sub>  |
|        | Tetrane . . . | C <sub>4</sub> H <sub>10</sub> | Nonane . . .  | C <sub>9</sub> H <sub>20</sub>  |
|        | Pentane . . . | C <sub>5</sub> H <sub>12</sub> | Decane . . .  | C <sub>10</sub> H <sub>22</sub> |

The whole series may be built up by progressive condensation, with simultaneous elimination of hydrogen, from the first term, Methane, CH<sub>4</sub> ; thus :



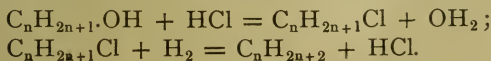
This condensation may be effected either directly by the agency of heat, or indirectly by the so-called method of addition, which consists, so to speak, in setting free, by appropriate means, two hydrocarbon residues of two monosubstitution-derivatives of C<sub>n</sub>H<sub>2n+2</sub> hydrocarbons in presence of each other, when they combine, thus :



The first of these methods is not generally available, inasmuch as the C<sub>n</sub>H<sub>2n+2</sub> hydrocarbons themselves lose hydrogen under the influence of heat. Various modifications of the second are therefore employed for their preparation.

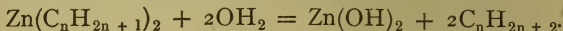
#### • GENERAL METHODS OF PREPARATION.

1. From the C<sub>n</sub>H<sub>2n+1</sub>.OH series of alcohols. These are converted by the action of the haloid acids, or haloid phosphorus compounds, into the corresponding monochlorinated, monobrominated, or moniodated paraffin, which is then submitted to the action of nascent hydrogen :

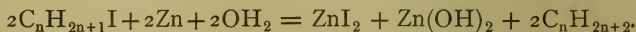


This is probably the only really general method of preparation ; those following all cease to be available at certain stages in the series.

2. By the action of water on the zinc organo-metallic compounds of the general formula  $\text{Zn}(\text{C}_n\text{H}_{2n+1})_2$  :



A modification of this method, whereby the previous preparation of the zinc organo-metallic compound in the pure state is avoided, consists in heating a mixture of the moniodo-derivative of the paraffin required with zinc and water :



3. By heating the moniodo-derivatives of the paraffins with zinc :



The paraffin thus formed is resolved partly, however, into the paraffin containing half as much carbon and the olefine<sup>1</sup> corresponding to it :



4. By the action of sodium on the moniodo-derivatives of the paraffins :



5. By the electrolysis of the acids of the  $\text{C}_n\text{H}_{2n+1}.\text{CO}_2\text{H}$  (or acetic) series :



6. By the dry distillation of a mixture of sodic hydrate with the sodic salt of an acid of the  $\text{C}_n\text{H}_{2n+1}.\text{CO}_2\text{H}$  (or acetic), or of the  $\text{C}_n\text{H}_{2n}(\text{CO}_2\text{H})_2$  (or succinic) series :

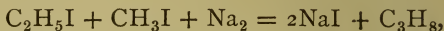


<sup>1</sup> The hydrocarbons of the  $\text{C}_n\text{H}_{2n}$  series are termed generically *Olefines*.

It is usual to regard the  $C_nH_{2n+2}$  series of hydrocarbons as derived from the first term, methane, by the substitution of so-called radicles of the  $C_nH_{2n+1}$  series for hydrogen. For example, ethane is regarded as formed from methane by the replacement of H in the latter by methyl ( $CH_3$ ); and the reaction whereby ethane is formed on treating iodomethane (methylic iodide) with sodium, viz. :  $2CH_3I + Na_2 = 2NaI + C_2H_6$ , may evidently be thus interpreted. On this view the names *methylmethane* and *dimethyl* are often applied to ethane, and have reference to the mode of formation indicated by the above equation. But these radicles of the  $C_nH_{2n+1}$  series, which are simply residues of  $C_nH_{2n+2}$  hydrocarbons, have no existence in the free state; in point of fact they are convenient fictions, which nevertheless render us great service in our system of symbolic notation. They are generally designated by names ending in *yl*, formed from the names of the hydrocarbons to which they correspond by changing the terminal *ane* into *yl*.

Methane and its homologues are also often regarded as compounds of  $C_nH_{2n+1}$  radicles with hydrogen, i.e. as hydrides of these radicles: thus methane is termed *methylic hydride*; ethane *ethylic hydride*, &c. This method of nomenclature, however, appears to suggest that a portion of the hydrogen in methane has a different value or function to that of the remaining hydrogen; now although this is not absolutely disproved by experiment, there is the strongest reason to believe that it is not the case, and it therefore appears unadvisable to regard these hydrocarbons as hydrides of hypothetical radicles. The names *dimethyl* and *methylmethane*, again, appear to suggest that ethane actually contains the radicle methyl, or that, in fact, when the two methyl groups liberated from  $2CH_3I$  by the action of  $Na_2$  coalesce to form  $C_2H_6$ , these groups still preserve their individuality in the new compound. If so, we should expect by the action of chlorine, for example,

on  $C_2H_6$ , to obtain  $2CH_3Cl$ ; this, however, is not the case, but chlorinated derivatives of  $C_2H_6$ , such as  $C_2H_5Cl$ , &c., are always produced. Again, the hydrocarbon  $C_3H_8$ , obtained by the action of sodium on a mixture of iodomethane and iodoethane :



does not yield a mixture of  $C_2H_5Cl$  and  $CH_3Cl$  when acted upon by chlorine, but such derivatives as  $C_3H_7Cl$  and  $C_3H_6Cl_2$ . Other reagents act similarly, and do not resolve the hydrocarbons into products bearing any simple relation to those from which they were originally built up.

We are thus led to conclude that these hydrocarbons are, so to speak, perfectly homogeneous compounds; that the so-called radicles from which they may conveniently be regarded as formed have on coalescing lost their individuality; in fact, that they have no real existence in the new compounds. From these considerations the name ethane appears therefore the most appropriate for the hydrocarbon obtained from iodomethane by the action of sodium; such names as methylmethane or dimethyl may still be usefully employed, in order to recall the operation whereby the compound is produced, although not as in any way expressing the actual constitution. Employed in this sense, such a system of symbolic nomenclature is of the greatest service, especially in the higher terms of the series, as a means of recalling the methods of formation of the compounds represented, and also of distinguishing between the numerous isomerides.

No isomeric modifications of the first three members of the series—methane,  $CH_4$ ; ethane,  $C_2H_6$ ; or propane,  $C_3H_8$ —have been obtained, but two modifications of the fourth member, tetraene,  $C_4H_{10}$ , are known, and each higher term of the series, so far as at present investigated, has been found capable of existing in a still greater number of

isomeric forms, the number of isomerides increasing more and more rapidly as the series is ascended.

Now according to the above view, which leads us to regard ethane as the mono-methyl-derivative of methane, no isomeric modifications of ethane are possible if the four units of hydrogen in methane are of exactly equal value, and, as a matter of fact, none have been obtained.

The next higher homologue, propane,  $C_3H_8$ , may be regarded as formed from methane by the substitution of hydrogen by ethyl,  $C_2H_5$ , the hypothetical radicle derived from ethane by the withdrawal of one unit-weight of hydrogen, and may be written  $CH_3.C_2H_5$  or  $CH_3.CH_2.CH_3$ , since  $C_2H_5$  equals  $CH_3.CH_3 - H = CH_3.CH_2$ . Propane is therefore ethylmethane, or, which is the same, methylethane. No other arrangement of the symbols being possible than that which obtains in the formula  $CH_3.CH_2.CH_3$ , there should be only one propane according to this theory, which is really the case. By replacing hydrogen in propane by methyl, the next higher homologue, methylpropane or tetrae,  $C_4H_{10}$ , is produced; but it will be evident that the formula of this hydrocarbon may be written in two ways: either H in one of the end  $CH_3$  groups may be supposed to be replaced by  $CH_3$ , as represented by the formula  $CH_3.CH_2.CH_2.CH_3$ , or the  $CH_3$  group may replace H in the centre  $CH_2$  group, whence the formula  $CH_3.CH(CH_3).CH_3$ ; and as a matter of fact two isomeric hydrocarbons of the composition  $C_4H_{10}$  are known. Similarly three isomeric pentanes,  $C_5H_{12}$ , have been prepared, and we find that the formula of this hydrocarbon may on the above theory be written in three ways, viz.:

1.  $CH_3.CH_2.CH_2.CH_2.CH_3$ .
2.  $CH_3.CH_2.CH(CH_3).CH_3$ .
3.  $C(CH_3)_4$ .

All other modes of arrangement appear on inspection to be identical with one or other of these.



Similarly it may be shown that the formula of Hexane,<sup>1</sup>  $C_6H_{14}$ , may be written in five, that of Heptane in nine, different ways ; and since three Hexanes and three Heptanes only are known, we anticipate that two modifications of the former and six modifications of the latter remain to be discovered.<sup>2</sup>

The operations whereby these isomeric hydrocarbons are produced are different, hence the isomerism ; and they are accordingly symbolised by differently constructed rational formulæ. It is in this sense, therefore, that the formulæ must be interpreted ; they are not to be regarded as representations of the actual constitution of the hydrocarbons.

The known paraffins may be classified in four series, according to their modes of formation and chemical behaviour. Those arranged in vertical columns in the accompanying table are *homologous*, those on the same horizontal line are *isomeric*.

The members of the first series are termed *normal primary paraffins* : they alone can be directly converted into normal primary monohydric alcohols. The boiling-point (and specific gravity in the liquid state) of each normal paraffin is, as a rule, higher than that of either of the corresponding isomeric hydrocarbons, and it is especially noteworthy that the normal paraffin is the term of greatest stability in each isomeric series ; it may be noticed also, that in their developed rational formulæ no one unit of carbon is represented

- |    |                                 |           |
|----|---------------------------------|-----------|
| 1. | $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$ |           |
| 2. | $CH_3.CH(CH_3).CH_2.CH_2.CH_3$  |           |
| 3. | $CH_3.CH(CH_3).CH(CH_3).CH_3$   |           |
| 4. | $CH_3.C(CH_3)_2.CH_2.CH_3$      | (unknown) |
| 5. | $CH_3.CH(C_2H_5).CH_2.CH_3$     | (unknown) |

<sup>2</sup> Prof. Cayley has calculated that no less than 799 paraffins of the formula  $C_{13}H_{28}$  are possible ; even supposing such a number to exist, however, it is probable that the differences between many would be so minute as to escape detection.



|                           |                                                                                                                                                                |                    | IV.                             |                                                   |                |                   |
|---------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|---------------------------------|---------------------------------------------------|----------------|-------------------|
| Name.                     | Formula.                                                                                                                                                       | Specific gravity.  | Name.                           | Formula.                                          | Boiling-point. | Specific gravity. |
| Methane .                 | $\text{CH}_4$                                                                                                                                                  |                    |                                 |                                                   |                |                   |
| Ethane . .                | $\text{C}_2\text{H}_6 = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \end{array}$                                                                      |                    |                                 |                                                   |                |                   |
| Propane . .               | $\text{C}_3\text{H}_8 = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                                                          |                    |                                 |                                                   |                |                   |
| Tetane . .<br>(Diethyl)   | $\text{C}_4\text{H}_{10} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                                                       |                    |                                 |                                                   |                |                   |
| Pentane . .               | $\text{C}_5\text{H}_{12} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                                      |                    | Tetramethyl-<br>methane . .     | $\text{C}(\text{CH}_3)_4$                         | 9°·5           |                   |
| Hexane . .<br>(Dipropyl)  | $\text{C}_6\text{H}_{14} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                                      | 58°<br>·670 at 17° | Ethyltrimethyl-<br>methane      | $\text{C}(\text{C}_2\text{H}_5)(\text{CH}_3)_3$   | 43°-48°        |                   |
| Heptane . .               | $\text{C}_7\text{H}_{16} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                     | —                  | Diethyldimethyl-<br>methane . . | $\text{C}(\text{C}_2\text{H}_5)_2(\text{CH}_3)_2$ | 86°-87°        | ·696 at 21°       |
| Octane . .<br>(Dibutyl)   | $\text{C}_8\text{H}_{18} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                     | 10°<br>·698 at 16° |                                 |                                                   |                |                   |
| Nonane . .                | $\text{C}_9\text{H}_{20} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$                     | 32°<br>·724 at 0°  |                                 |                                                   |                |                   |
| Decane . .                | $\text{C}_{10}\text{H}_{22} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$ | 58°<br>·727 at 14° |                                 |                                                   |                |                   |
| Endecane .                | $\text{C}_{11}\text{H}_{24} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$ |                    |                                 |                                                   |                |                   |
| Dodecane .<br>(Dihexyl)   | $\text{C}_{12}\text{H}_{26} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$ |                    |                                 |                                                   |                |                   |
| Tridecane .               | $\text{C}_{13}\text{H}_{28}$                                                                                                                                   |                    |                                 |                                                   |                |                   |
| Tetradecane               | $\text{C}_{14}\text{H}_{30}$                                                                                                                                   |                    |                                 |                                                   |                |                   |
| Pentadecane               | $\text{C}_{15}\text{H}_{32}$                                                                                                                                   |                    |                                 |                                                   |                |                   |
| Hexadecane .<br>(Dioctyl) | $\text{C}_{16}\text{H}_{34} = \begin{array}{c}   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \\   \\ \text{C} \end{array}$ |                    |                                 |                                                   |                |                   |

able that the relations in boiling-point and specific gravity (and other homologous and isomeric paraffins are in reality much more definite To ascertain the true relations, however, it will be necessary to compare pure compounds at the same temperature, and their boiling-points over, it will be necessary that the latter be given in terms of the air table standard than the mercurial thermometer.

*Table of Homologous and Isomeric Paraffins.*

To face page 76.

| I.                       |                                                                                                                             |                |                       | II.                                                               |                                                                                                                        |                                                     |                                                                                             | III.             |                                                                                                                                                   |                |                   | IV.                              |                                                                                |                |                   |
|--------------------------|-----------------------------------------------------------------------------------------------------------------------------|----------------|-----------------------|-------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|---------------------------------------------------------------------------------------------|------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|----------------|-------------------|----------------------------------|--------------------------------------------------------------------------------|----------------|-------------------|
| Name.                    | Formula.                                                                                                                    | Boiling-point. | Specific gravity.     | Name.                                                             | Formula.                                                                                                               | Boiling-point.                                      | Specific gravity.                                                                           | Name.            | Formula.                                                                                                                                          | Boiling-point. | Specific gravity. | Name.                            | Formula.                                                                       | Boiling-point. | Specific gravity. |
| Methane .                | CH <sub>4</sub>                                                                                                             |                |                       |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Ethane .                 | C <sub>2</sub> H <sub>6</sub> = $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$                              |                |                       |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Propane .                | C <sub>3</sub> H <sub>8</sub> = $\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$          |                |                       |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Tetrane . .<br>(Diethyl) | C <sub>4</sub> H <sub>10</sub> = $\begin{array}{c} (\text{CH}_2)_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$     | 1°             | '600 at 0°            | Trimethylmethane . .<br>(Methylisopropyl)                         | CH(CH <sub>3</sub> ) <sub>3</sub>                                                                                      | -15°                                                |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Pentane .                | C <sub>5</sub> H <sub>12</sub> = $\begin{array}{c} (\text{CH}_2)_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$     | 38°            | '628 at 17°           | Ethylidimethylmethane<br>(Ethylisopropyl)                         | $\begin{array}{c} \text{CH}(\text{CH}_3)_2 \\   \\ \text{C}_2\text{H}_5 \end{array}$                                   | 30°                                                 | —                                                                                           |                  |                                                                                                                                                   |                |                   | Tetramethyl-<br>methane . .      | C(CH <sub>3</sub> ) <sub>4</sub>                                               | 9°·5           |                   |
| Hexane . .<br>(Dipropyl) | C <sub>6</sub> H <sub>14</sub> = $\begin{array}{c} (\text{CH}_2)_4 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$     | 70°            | '669 at 16°           | Propyldimethylmethane<br>(Ethylisobutyl)                          | $\begin{array}{c} \text{CH}(\text{CH}_3)_2 \\   \\ \text{C}_3\text{H}_7 \end{array}$                                   | 62°                                                 | '701 at 0°                                                                                  | Diisopropyl . .  | $\begin{array}{c} \text{CHC}(\text{H}_3)_2 \\   \\ \text{CH}(\text{CH}_3)_2 \end{array}$                                                          | 58°            | '670 at 17°       | Ethyltrimethyl-<br>methane       | C(C <sub>2</sub> H <sub>5</sub> )(CH <sub>3</sub> ) <sub>3</sub>               | 43°-48°        |                   |
| Heptane .                | C <sub>7</sub> H <sub>16</sub> = $\begin{array}{c} (\text{CH}_2)_5 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$     | 99°            | '699 at 15°           | Triethylmethane . . .<br>Tetryldimethylmethane<br>(Ethylisooamyl) | $\begin{array}{c} \text{CH C}(\text{H}_3)_3 \\   \\ \text{CH}(\text{CH}_3)_2 \\   \\ \text{C}_4\text{H}_9 \end{array}$ | $\begin{array}{c} 66^\circ \\ 91^\circ \end{array}$ | $\begin{array}{c} '683 \text{ at } 27^\circ \\ '683 \text{ at } 18^\circ\cdot4 \end{array}$ | —                | —                                                                                                                                                 | —              | —                 | Diethylidimethyl-<br>methane . . | C(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> | 86°-87°        | '696 at 21°       |
| Octane . .<br>(Dibutyl)  | C <sub>8</sub> H <sub>18</sub> = $\begin{array}{c} (\text{CH}_2)_6 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$     | 124°           | '726 at 15°           | —                                                                 | —                                                                                                                      | —                                                   | —                                                                                           | Diisobutyl . .   | $\begin{array}{c} \text{CH}(\text{CH}_3)_3 \\   \\ (\text{CH}_2)_3 \\   \\ \text{CH}(\text{CH}_3)_3 \end{array}$                                  | 110°           | '698 at 16°       |                                  |                                                                                |                |                   |
| Nonane .                 | C <sub>9</sub> H <sub>20</sub> = $\begin{array}{c} (\text{CH}_2)_7 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$     | 148°           | '728 at 13°·5         | —                                                                 | —                                                                                                                      | —                                                   | —                                                                                           | Isobutylisooamyl | $\begin{array}{c} \text{CH}(\text{CH}_3)_2 \\   \\ (\text{CH}_2)_3 \\   \\ \text{CH}(\text{CH}_3)_2 \end{array}$                                  | 132°           | '724 at 0°        |                                  |                                                                                |                |                   |
| Decane .                 | C <sub>10</sub> H <sub>22</sub> = $\begin{array}{c} (\text{CH}_2)_8 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$    | 166-168°       | '739 at 13°·5         | —                                                                 | —                                                                                                                      | —                                                   | —                                                                                           | Diisooamyl . .   | $\begin{array}{c} \text{CH}(\text{CH}_3)_2 \\   \\ \text{CH}(\text{CH}_3)_2 \\   \\ (\text{CH}_2)_4 \\   \\ \text{CH}(\text{CH}_3)_2 \end{array}$ | 158°           | '727 at 14°       |                                  |                                                                                |                |                   |
| Endecane                 | C <sub>11</sub> H <sub>24</sub> = $\begin{array}{c} (\text{CH}_2)_9 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$    | 180-184°       | '765 at 16°           |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Dodecane<br>(Dihexyl)    | C <sub>12</sub> H <sub>26</sub> = $\begin{array}{c} (\text{CH}_2)_{10} \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$ | 202°           | '774 at 17°           |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Tridecane                | C <sub>13</sub> H <sub>28</sub>                                                                                             | 216-218°       | '792 at 20°           |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Tetradecane              | C <sub>14</sub> H <sub>30</sub>                                                                                             | 236-240°       | —                     |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Pentadecane              | C <sub>15</sub> H <sub>32</sub>                                                                                             | 258-262°       | '825 at 16°           |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |
| Hexadecane<br>(Diocetyl) | C <sub>16</sub> H <sub>34</sub> = $\begin{array}{c} (\text{CH}_2)_{14} \\   \\ \text{CH}_2 \end{array}$                     | 278°           | solid<br>melts at 21° |                                                                   |                                                                                                                        |                                                     |                                                                                             |                  |                                                                                                                                                   |                |                   |                                  |                                                                                |                |                   |

NOTE.—It is more than probable that the relations in boiling-point and specific gravity (and other physical properties) between the homologous and isomeric paraffins are in reality much more definite than appears from this table. To ascertain the true relations, however, it will be necessary to compare the specific gravities of the pure compounds at the same temperature, and their boiling-points under the same pressure; moreover, it will be necessary that the latter be given in terms of the air the barometer, or some more reliable standard than the mercurial thermometer.

as directly united with more than two other units of carbon, or, to use symbolic language, 'the carbon atoms are united in a single chain.' It will be seen that the difference, at first  $37^{\circ}$ , between the boiling-point of the homologous terms in this series decreases regularly by about  $4^{\circ}$ ; there is reason to believe that after octane the difference becomes a constant one of  $19^{\circ}$ , since the boiling-points of *dodecane* and *hexdecane*, the only two members of the series after octane with which we are well acquainted, are in agreement with this assumption. Doubtless similar relations obtain between the boiling-points of the homologues in the second, third, and fourth series. Thus in the second division, each addition of  $\text{CH}_2$  to the formula corresponds to a rise of about  $31^{\circ}$  in boiling-point; in the third, there is a mean difference of about  $25^{\circ}$ ; whilst in the fourth, the difference would seem to be much greater, viz., about  $38^{\circ}$ . Our knowledge of the paraffins of these three series is, however, extremely deficient, and probably but few of the boiling-points quoted are exact, since the observations have been made by various chemists using different instruments, and often very small quantities of substance.

The normal paraffins are contained in petroleum oil and in the paraffin oils obtained by distilling coal, Boghead cannel, &c. They have also been obtained synthetically by the above-mentioned general methods of preparation: especially by the first general method from the normal primary and normal secondary monohydric alcohols, and by the fourth method by the action of sodium on a pure iodide, or mixture of two iodides (moniodoparaffins) derived from the normal primary monohydric alcohols of the  $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$  series.<sup>1</sup>

<sup>1</sup> Having regard to the formation of normal paraffins from both normal primary and normal secondary monohydric alcohols, it is a remarkable fact that the normal paraffins (pentane, hexane, and heptane, and probably their homologues also) yield a mixture of two isomeric monochlorinated derivatives when acted upon by chlorine, one of

Some at least of the paraffins of the second series are present in petroleum oil, but our chief knowledge of this group has been derived from the study of the various members obtained by synthetic methods.

In the preparation of the members of the third and fourth series, synthetic methods alone have been employed.

In each homologous series a diminution in stability is observed as the boiling-point rises; the higher hydrocarbons exhibit, especially in their mono-haloid derivatives and corresponding alcohols, a gradually increasing tendency to split up into the corresponding olefine ( $C_nH_{2n}$ ) and hydrogen, haloid acid, or water. In each isomeric series, however, the alteration in stability is in the contrary direction: the isomeric of lower boiling-point being far more readily decomposed than that of higher boiling-point, and this behaviour is equally characteristic of the derivatives.

As already stated, it appears that in each isomeric (horizontal) series, the normal paraffin possesses relatively the highest specific gravity and boiling-point. Now Berthelot has pointed out that in the case of compounds of identical composition, but of different specific gravity and boiling-point, more heat is evolved in the formation of the compound of higher, than in the formation of the compound of lower specific gravity and boiling-point. Thus, on combustion of 60 grammes of methylic formate, which boils at  $33^\circ$ , and at  $15^\circ$  has a specific gravity of  $\cdot977$ , 252,000 units of heat are evolved; whereas on combustion of the same quantity of acetic acid, which has the same composition, but the specific gravity  $1\cdot063$  at  $15^\circ$ , and which boils at  $117^\circ$ , only 210,000 heat-units are set free, showing that considerably less heat must be evolved in the formation of methylic formate than in the formation of the metameric body, acetic acid.

Hence, although the necessary data for the calculation of which is convertible into the corresponding normal primary, the other into the normal secondary monohydric alcohol.

the amount of heat evolved in the formation, or on combustion, of the isomeric paraffins have not yet been obtained, there is on this account reason to believe that more heat is evolved in the formation of the primary paraffin than in the formation of either of the isomerides. This conclusion is strongly supported by the difference in chemical behaviour which the isomeric paraffins exhibit, inasmuch as it at once suffices to explain the superior stability of the normal paraffins and their derivatives.

The paraffins are for the most part an extremely inert series of bodies ; they are not acted upon by sulphuric acid, nor by cold concentrated nitric acid, but are oxidised by prolonged boiling with the latter acid. Other oxidising agents have also little or no action on the paraffins in the cold ; on heating they slowly determine their conversion for the greater part into carbonic anhydride and water, whilst at the same time relatively small quantities of acids of the  $C_nH_{2n+1}(CO_2H)$  and  $C_nH_{2n}(CO_2H)_2$  series are produced.

METHANE (methylic hydride ; marsh-gas ; light carburated hydrogen ; fire-damp),  $CH_4$ .

*Occurrence.*—1. As a product of the decomposition of organic substances out of contact with air. 2. In coal mines. 3. In volcano gases ; the gas of the mud volcano at Bulganak in the Crimea is nearly pure methane.

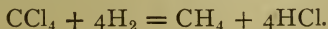
*Preparation.*—1. By passing carbonic disulphide vapour and hydric sulphide (or steam) over red-hot copper :



2. By the action of water on zincic methide :



3. By the action of nascent hydrogen on carbonic tetrachloride ( $CCl_4$ ), chloroform ( $CHCl_3$ ), or iodoform ( $CHI_3$ ) :





4. By heating a mixture of sodic acetate and soda-lime :



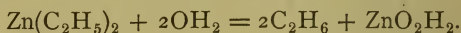
The mixture of one part sodic acetate and two parts soda lime is carefully heated in a hard glass retort or tube, or copper flask, and the evolved gas passed through a solution of sodic hydrate and afterwards through concentrated sulphuric acid. The gas thus obtained is not pure methane, but contains traces of higher hydrocarbons, of acetone, &c.; in fact, pure methane is only obtained by method 2.

5. By the destructive distillation of organic substances such as wood, coal, &c., but together with a variety of other hydrocarbons ; hence it is a constituent of coal-gas.

*Properties.*—Methane is a colourless, odourless, inflammable, uncondensable gas, sparingly soluble in water, more soluble in alcohol ; it burns with a scarcely luminous flame, and a mixture of it with oxygen or air explodes violently on ignition. A mixture of methane and chlorine explodes on exposure to direct sunlight, or on passing an electric spark through it— $\text{CH}_4 + 2\text{Cl}_2 = \text{C} + 4\text{HCl}$  ; but in diffused light the action of chlorine gives rise to the formation of mono-, di-, tri-, and tetra-chloromethane,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ .

ETHANE (ethylic hydride ; dimethyl),  $\text{C}_2\text{H}_6$ .

- Preparation.*—1. By the action of water on zincic ethide :



2. By the electrolysis of acetic acid :



The hydrogen is evolved at the negative pole, the ethane and carbonic anhydride together at the positive pole. The apparatus is therefore so arranged that the gaseous products can be collected separately. The positive pole consists of a platinum plate suspended in a cylinder of porous earthenware, the open end of which is closed by a cork perforated by the pole wire affixed to the platinum plate and by a narrow glass tube ; the porous cylinder stands in a glass cell and is surrounded by a sheet of copper, serving as negative pole. The cylinder and glass cell are

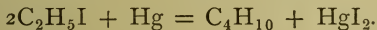
filled with a solution of potassic acetate. The zinc terminal of a battery of 4 or 6 powerful Bunsen or Grove cells is then connected with the copper plate, and the carbon or platinum terminal with the platinum plate. The gas evolved in the porous cell is passed through a bulb apparatus containing potassic hydrate solution, to remove carbonic anhydride; afterwards through fuming sulphuric acid, to free it from traces of ethylene; then through potassic hydrate solution and concentrated sulphuric acid, and is finally collected over mercury.

*Properties.* — Ethane is a colourless, inodorous gas, scarcely soluble in water, but dissolved by alcohol to the extent of 1.22 of the volume of the latter (at  $8.8^{\circ}$ ). It does not liquefy at  $-18^{\circ}$ , or even under a pressure of 20 atmospheres. By the action of chlorine in diffused light it is converted into chlorinated derivatives,  $C_2H_5Cl$ ,  $C_2H_4Cl_2$ , &c. Bromine is without action on it even in bright sunlight.

PROPANE,  $C_3H_6$ , may be obtained by the action of nascent hydrogen either on  $\alpha$ -chloropropane (propylic chloride),  $CH_3.CH_2.CH_2Cl$ , or on  $\beta$ -chloropropane (isopropylic chloride),  $CH_3.CHCl.CH_3$ ; and also by the fourth, fifth, and sixth general methods of preparation.

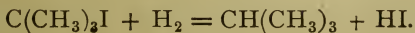
TETRANE,  $C_4H_{10}$ .—As already stated, two modifications of this paraffin exist, viz. :—

*Normal Tetrane, or Diethyl*,  $CH_3.CH_2.CH_2.CH_3$ .—Preparation :—By general methods. A remarkable special method consists in exposing iodethane (ethylic iodide) over mercury to the influence of bright sunlight :



Normal tetrane boils at  $1^{\circ}$ .

*Isopropylmethane, or Trimethylmethane*,  $CH_3.CH(CH_3).CH_3$ , is obtained by the action of nascent hydrogen on the iodotetrane formed from trimethylcarbinol (tertiary butylic alcohol) :





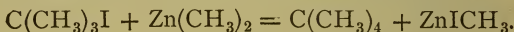
The boiling-point of this hydrocarbon is  $-15^{\circ}$ .

PENTANE,  $C_5H_{12}$ .—The first of the three modifications of this hydrocarbon, *normal pentane*,  $CH_3.CH_2.CH_2.CH_2.CH_3$ , is obtained from petroleum oil ; the second, *isopropylethane*,  $CH_3.CH(CH_3).CH_2.CH_3$ , is prepared by the action of nascent hydrogen on  $\beta$ -iodopentane prepared from fermentation amylic alcohol, or by the action of sodium on a mixture of iodethane and  $\beta$ -iodopropane (isopropyl iodide) :



Normal pentane boils at  $38^{\circ}$  ; isopropylethane at  $30^{\circ}$ .

*Tetramethylmethane*,  $C(CH_3)_4$ , the third modification of pentane, has been obtained by the action of zinc methide on the iodotetrane formed from trimethylcarbinol :



It is a colourless liquid, which boils at  $9^{\circ}5$  and solidifies at  $-20^{\circ}$  to a white crystalline mass.

By oft-repeated fractional distillation, members of the paraffin series up to  $C_{15}H_{32}$  have been isolated from petroleum oil, which doubtless contains terms of a still higher order. Mixtures of the liquid hydrocarbons of the series—known in commerce as *paraffin oil*, *photogene*, *solar oil*, &c.—are extensively used as illuminating agents, and the higher terms, which are of an oily or buttery consistency, for lubricating machinery ; such mixtures are now largely manufactured by destructive distillation of Boghead and cannel coal, lignite, asphalte, &c.

*Paraffin*.—The white solid substance known under this name is probably a mixture of several members of the  $C_nH_{2n+2}$  series, in which the value of  $n$  has not been satisfactorily determined. It is produced, together with the lower liquid terms of the series, by the destructive distillation of Boghead or cannel coal, &c. The purification of the crude distillate is a matter of considerable difficulty, the following being an outline of one of the processes employed:—

The crude tar resulting from the first distillation is separated from the water produced simultaneously, and redistilled; the distillate is then placed in large closed cast-iron vessels, and thoroughly agitated with a solution of sodic hydrate, in order to remove the acid substances which it contains. After standing some time the oil is separated, washed with water, and then treated with concentrated sulphuric acid in the same manner, in order to free it from all basic substances, naphthalene, &c.; it is next separated from the acid, washed, first with water, then with weak soda-lye, then distilled, and the portion of the distillate which becomes solid on cooling collected apart. This crude product is placed in a centrifugal machine, whereby a quantity of thick oil is expressed; then cast into cakes, and subjected to hydraulic pressure, first in the cold and afterwards at  $35^{\circ}$ – $40^{\circ}$ , in order to remove all hydrocarbons melting below  $40^{\circ}$ . The pressed paraffin is next heated with a small quantity of concentrated sulphuric acid at  $150^{\circ}$ , whereby the hydrocarbons other than paraffins are carbonised, the paraffin remaining unaltered; it is then carefully washed, dissolved in the oils of low boiling-point, the hot solution filtered through animal charcoal to remove colouring matter, and the volatile oil distilled off.

Thus prepared, it is colourless and translucent, melting at  $40^{\circ}$ – $60^{\circ}$ , according to the source from which it is obtained; it boils at about  $370^{\circ}$ .

It has recently been shown<sup>1</sup> that when such paraffin is heated for some time to a high temperature under pressure, it is resolved into a complex mixture of liquid hydrocarbons, members of the  $C_nH_{2n+2}$  and  $C_nH_{2n}$  series.

Heated for several days with a mixture of sulphuric acid and potassic dichromate solution, it is converted mainly into *cerotic acid*,  $C_{27}H_{54}O_2$ , whilst on oxidation with nitric acid it yields a mixture of solid and liquid fatty acids (acids of the  $C_nH_{2n+1}\cdot CO_2H$  or acetic series), together with *succinic* and, perhaps, *anchoic* acid.

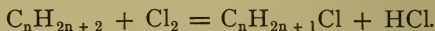
The minerals known as fossil wax, ozokerit, &c., found in the coal measures, contain paraffins of high melting-point.

<sup>1</sup> Thorpe and Young, *Proceedings of the Royal Society*, vol. xx. p. 488.

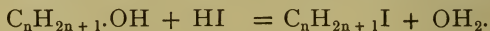
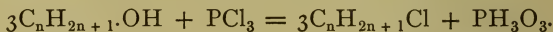
## HALOID DERIVATIVES OF THE PARAFFINS.

The paraffins are all acted upon by chlorine, and converted into substitution-derivatives, more especially under the influence of sunlight; the presence of a small quantity of iodine also often facilitates the action of chlorine. Bromine, in most cases, acts similarly, though less energetically. Iodine, so far as is known, has no direct action on them.

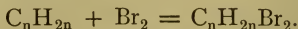
In the preparation of the mono-substitution derivatives higher substituted products are always formed simultaneously, even when chlorine (or bromine) and the hydrocarbon are employed exactly in the proportions required by the equation :



Thus, when a mixture of equal volumes of chlorine and methane is exposed to diffused light, together with  $\text{CH}_3\text{Cl}$ , more or less  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ , according to the conditions of experiment, are always obtained; a certain quantity of methane, therefore, necessarily remains unattacked. On this account the pure mono-haloid derivatives are most conveniently prepared from the corresponding monohydric alcohols by the action of the haloid phosphorus compounds, or of the haloid acids, according to such general reactions as the following equations express :—



Pure di-derivatives of the paraffins are obtained from the  $\text{C}_n\text{H}_{2n}$  series of hydrocarbons, which combine directly with the halogens, thus :



The compounds so produced are sometimes identical, sometimes isomeric with those obtained by the direct action of the halogens on the paraffins from which the olefines em-

ployed are derived: thus, dichlorethane,  $C_2H_4Cl_2$ , from ethane, is isomeric with the body formed by the direct addition of chlorine to ethylene,  $C_2H_4$ ; but dichloropropane,  $C_3H_6Cl_2$ , from propane, is identical with the body obtained by the direct combination of propylene,  $C_3H_6$ , with chlorine.

The higher haloid derivatives of the paraffins, excepting those derived from methane and ethane, have been little studied.

As already stated, two isomeric mono-haloid derivatives are formed simultaneously by the action of chlorine on the normal primary paraffins (pentane, hexane, and heptane<sup>1</sup>), convertible respectively into a normal primary and a normal secondary monohydric alcohol; the derivative yielding the former may be termed the  $\alpha$ -derivative, and that yielding the latter the  $\beta$ -derivative.<sup>2</sup> In the following tables the boiling-points and specific gravities in the liquid state of the known  $\alpha$ - and  $\beta$ -monochloro-, monobromo-, and moniodo-derivatives of the first eight normal primary paraffins are given:—

*Boiling-points.*

| Formula       | $\alpha$ -derivs. | $\beta$ -derivs. | Formula       | $\alpha$ -derivs. | $\beta$ -derivs. | Formula      | $\alpha$ -derivs. | $\beta$ -derivs. |
|---------------|-------------------|------------------|---------------|-------------------|------------------|--------------|-------------------|------------------|
|               | °                 | °                |               | °                 | °                |              | °                 | °                |
| $CH_3Cl$      | —                 | —                | $CH_3Br$      | 13                | —                | $CH_3I$      | 40                | —                |
| $C_2H_5Cl$    | 12·5              | —                | $C_2H_5Br$    | 41                | —                | $C_2H_5I$    | 72·5              | —                |
| $C_3H_7Cl$    | 46·5              | 39               | $C_3H_7Br$    | 71                | 61               | $C_3H_7I$    | 102               | 89·5             |
| $C_4H_9Cl$    | 77·5              | 70               | $C_4H_9Br$    | 100·5             | 90·5             | $C_4H_9I$    | 129·5             | 120·5            |
| $C_5H_{11}Cl$ | 106·5             | 101              | $C_5H_{11}Br$ | 129               | 121              | $C_5H_{11}I$ | 155·5             | 147·5            |
| $C_6H_{13}Cl$ | —                 | —                | $C_6H_{13}Br$ | —                 | —                | $C_6H_{13}I$ | 179·5             | 167·5            |
| $C_7H_{15}Cl$ | —                 | —                | $C_7H_{15}Br$ | —                 | —                | $C_7H_{15}I$ | —                 | —                |
| $C_8H_{17}Cl$ | 180               | 175              | $C_8H_{17}Br$ | 199               | —                | $C_8H_{17}I$ | 221               | 211              |

<sup>1</sup> It appears probable that all the homologous normal primary paraffins from propane inclusive upwards exhibit a similar behaviour. The behaviour of their isomerides with chlorine has been little studied as yet, but it may be expected that in many cases it will be found that isomeric derivatives are also formed simultaneously from them.

<sup>2</sup> The action of chlorine on these paraffins is thus complementary to that of haloid acids on the isomeric normal primary and secondary

## Specific Gravities.

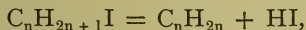
| Formula                            | $\alpha$ -derivatives | $\beta$ -derivatives |
|------------------------------------|-----------------------|----------------------|
| $\text{CH}_3\text{Cl}$             | —                     | —                    |
| $\text{C}_2\text{H}_5\text{Cl}$    | ·920 at $0^\circ$     | —                    |
| $\text{C}_3\text{H}_7\text{Cl}$    | ·915 „                | ·874 at $10^\circ$   |
| $\text{C}_4\text{H}_9\text{Cl}$    | ·907 „                | ·895 „ 0             |
| $\text{C}_5\text{H}_{11}\text{Cl}$ | ·901 „                | ·886 „ 0             |
| $\text{C}_6\text{H}_{13}\text{Cl}$ | —                     | —                    |
| $\text{CH}_3\text{Br}$             | —                     | —                    |
| $\text{C}_2\text{H}_5\text{Br}$    | 1·47 at $0^\circ$     | —                    |
| $\text{C}_3\text{H}_7\text{Br}$    | 1·35 „ 16             | 1·32 at 13           |
| $\text{C}_4\text{H}_9\text{Br}$    | 1·30 „ 0              | 1·24 „ 0             |
| $\text{C}_5\text{H}_{11}\text{Br}$ | 1·22 „ 20             | 1·21 „ 16            |
| $\text{C}_6\text{H}_{13}\text{Br}$ | —                     | —                    |
| $\text{CH}_3\text{I}$              | 2·19 at 0             | —                    |
| $\text{C}_2\text{H}_5\text{I}$     | 1·97 „ 0              | —                    |
| $\text{C}_3\text{H}_7\text{I}$     | 1·76 „ 16             | 1·70 at 15           |
| $\text{C}_4\text{H}_9\text{I}$     | 1·64 „ 0              | 1·63 „ 0             |
| $\text{C}_5\text{H}_{11}\text{I}$  | 1·54 „ 0              | 1·46 „ 0             |
| $\text{C}_6\text{H}_{13}\text{I}$  | 1·41 „ 17             | 1·44 „ 0             |

Inspection of these tables shows that the relations between the isomeric mono-haloid derivatives of the paraffins are of the same nature as those observed to exist between the isomeric paraffins. The  $\alpha$ -derivative has a higher boiling-point and in most (probably in all) cases also a higher specific gravity than the corresponding  $\beta$ -derivative ; and it will be noticed (more especially in the case of the iodo-derivatives) that the difference in boiling-point between every two successive homologues diminishes steadily as the series is ascended. It appears probable<sup>1</sup> that when the difference has sunk to about  $19^\circ$  it becomes constant.

alcohols, which yield mono-haloid derivatives—isomeric among themselves, but convertible by the action of nascent hydrogen into the same normal primary paraffin.

<sup>1</sup> Schorlemmer, *Memoirs of the Manchester Philosophical Society*, 1871-2, p. 115.

Only two monochloro- (bromo- and iodo-) derivatives of propane are known, but a far greater number of monohaloid derivatives of the homologous paraffins are obtainable : thus, for example, four isomeric moniodotetranes are known. In the case of all such isomeric derivatives, however, the relations are of precisely the same character as above indicated for the  $\alpha$ - and  $\beta$ -derivatives: the compounds of highest and lowest boiling-point in each isomeric series possess respectively the highest and lowest specific gravity, the boiling-points and specific gravities of the intermediate compounds being similarly related. But it is a most noteworthy circumstance, illustrating clearly the correlation which undoubtedly exists between the physical and chemical properties of compounds, that as the boiling-point and specific gravity of the successive terms in the isomeric series fall, so does the stability appear to diminish, for whereas the members of lowest boiling-point are split up with comparative ease (even by a moderate degree of heat alone in some cases) into the olefine and haloid acid, thus :



those of highest boiling-point (the  $\alpha$ -derivatives) undergo this decomposition far less readily ; and apparently also in reactions of double decomposition the haloid derivatives of high boiling-point enter into reaction less readily than their isomerides of lower boiling-point : a higher temperature, or more prolonged contact between the substances, being usually required to effect the chemical change.

In the following several of the more important haloid derivatives of the paraffin methane are specially described :—

*Monochloromethane (Methylic Chloride),*  $CH_3Cl$ . — This compound is the first product of the action of chlorine on methane in diffused light, but it is best prepared by saturating well-cooled methylic alcohol ( $CH_3.OH$ ) with hydrochloric acid gas ; on gently heating the product chloromethane is evolved as a colourless gas.

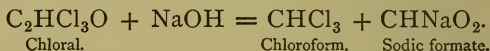


*Dichloromethane* (*Methylene Chloride*),  $\text{CH}_2\text{Cl}_2$ .—This is the first product of the action of chlorine in sunshine on monochloromethane. It is a colourless liquid of sp. gr. 1.36, boiling at  $40^\circ$ – $42^\circ$ .

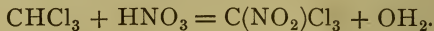
*Trichloromethane* (*Chloroform*),  $\text{CHCl}_3$ .—Though it may be obtained by the action of chlorine on methane, chloroform is never prepared on the large scale by that method, but by the action of the so-called bleaching powder (chloride of lime) on alcohol.

*Preparation*.—About 80 lbs. of the strongest chloride of lime are introduced, together with about 8 lbs. of slaked lime and 22 gallons of water, at a temperature of  $80^\circ$ – $90^\circ$ , into a wooden cask or large leaden vessel; the whole having been thoroughly mixed, 2 lbs. of alcohol are poured in. The heat evolved in the reaction is usually sufficient to cause the chloroform to distil over after a short time, but if not, a current of steam is passed into the vessel. The precise reaction which occurs in this process is not known.

Chloroform is also obtained by the action of alkalies on chloral and several other highly-chlorinated compounds :



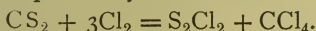
It is a colourless, mobile liquid, of peculiarly sweet taste and smell; sp. gr. 1.5; boiling-point  $62^\circ$ . It is largely employed as an anæsthetic, but is also a very valuable solvent. When heated with concentrated nitric acid for some time at  $100^\circ$  it is converted into *chloropicrin* (nitrotrichloromethane)  $\text{C}(\text{NO}_2)\text{Cl}_3$  :



Chloropicrin is also a constant product of the action of bleaching powder on organic nitro-compounds, and is most readily obtained by distilling trinitrophenol with that substance and water. It is a colourless, mobile, heavy liquid (sp. gr. 1.66), which boils at  $112^\circ$ . It has a most powerful and irritating odour, mere traces of its vapour exciting a copious flow of tears.

*Triiodomethane (Iodoform)*,  $\text{CHI}_3$ , is a product of the action of iodine, in presence of potassic hydrate, on various organic substances, such as alcohol, acetone, sugar, &c. It crystallises in pale yellow six-sided plates, easily soluble in alcohol

*Tetrachloromethane (Carbonic Tetrachloride)*,  $\text{CCl}_4$ .—This body may be obtained by the action of chlorine in sunlight on chloroform, but it is most easily prepared by passing a current of dry chlorine into gently-heated carbonic disulphide, to which a small quantity of iodine or antimonie pentachloride has previously been added :



It is a colourless, heavy, mobile liquid, much resembling chloroform, and, like it, possesses anæsthetic properties ; sp. gr. 1.6 ; boiling-point  $78^\circ$ . By the action of nascent hydrogen (from sodium amalgam and water), tetrachloromethane may successively be reduced to tri-, di-, and monochloromethane, and finally to methane itself.

*Tetrabromomethane*,  $\text{CBr}_4$ , is formed on heating triiodomethane with an excess of bromine at about  $180^\circ$  ; it crystallises in shining plates melting at  $91^\circ$ .

*Tetriadomethane*,  $\text{CI}_4$ , is formed by the action of aluminic iodide on tetrachloromethane ; it crystallises in regular octohedrons.

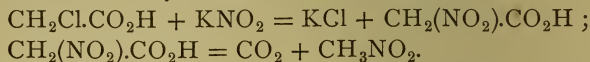
#### NITRO-DERIVATIVES OF THE PARAFFINS.

These derivatives cannot be obtained by the direct action of nitric acid on the lower paraffins, but are readily prepared by the action of their moniodo-derivatives on argentic nitrite. It is said, however, that the higher terms of the series are acted upon by nitric acid, and converted into nitro-derivatives, octane, for example, yielding *nitro-octane*,  $\text{C}_8\text{H}_{17}(\text{NO}_2)$ , but this requires confirmation.

*Nitromethane*,  $\text{CH}_3(\text{NO}_2)$ .—Iodomethane (methylic iodide) reacts with great violence on argentic nitrite, and is entirely converted into nitromethane :

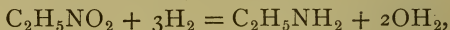


Nitromethane is also obtained by the action of potassic nitrite on monochloroacetic acid. In this case, probably, a mononitroacetic acid is first formed, but at once decomposed into carbonic anhydride and nitromethane :

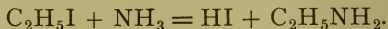


Nitromethane is a heavy, oily liquid of peculiar odour, which boils at  $99^\circ$  ; the metameric compound, methylic nitrite,<sup>1</sup> boils at  $-12^\circ$ . If mixed with an alcoholic solution of sodic hydrate, it is converted into a white crystalline sodium-derivative of the formula  $\text{CH}_2\text{NaNO}_2$ . Chlorine has no action on it even in bright sunlight, but if distilled with chloride of lime it is converted into *chloronitromethane*,  $\text{CH}_2\text{ClNO}_2$ , a heavy liquid, closely resembling chloropicrin in odour. *Nitroethane*,  $\text{C}_2\text{H}_5\text{NO}_2$ , is obtained by the action of iodoethane (ethylic iodide) on argentic nitrite, but at the same time a quantity of the metameric ethylic nitrite (B.P.  $16^\circ$ ) is produced. It is a colourless, highly-refractive liquid, insoluble in water, boiling at  $111^\circ$ – $113^\circ$ . By the action of sodium, or of an alcoholic solution of sodic hydrate, it is converted into  $\text{C}_2\text{H}_4\text{NaNO}_2$ .

By the action of nascent hydrogen nitroethane is converted into amidoethane (ethylamine) :



identical with the product of the action of ammonia on iodoethane :



Nitro-derivatives of several of the higher paraffins have been obtained by similar means.

#### CYANO-DERIVATIVES OF THE PARAFFINS.

When iodoethane and potassic cyanide are heated together, double decomposition occurs ( $\text{C}_2\text{H}_5\text{I} + \text{KCN} = \text{KI} + \text{C}_2\text{H}_5.\text{CN}$ ), but the product is a mixture of two liquid sub-

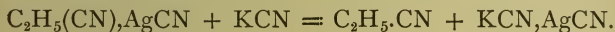
<sup>1</sup> Obtained by the action of nitrous acid on methylic alcohol.

stances of like composition, possessing totally distinct properties, however ; the one of which has a slight alliaceous odour and boils at  $96.5^{\circ}$ , whilst the other has a most intolerable odour and boils at  $78^{\circ}$ – $79^{\circ}$ .

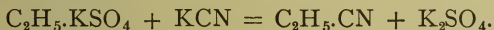
A similar result is obtained when argentic cyanide is employed, but the product then consists in the main of the compound of lower boiling-point : in the first place, a double compound of argentic cyanide with the cyano-derivative is formed, thus :



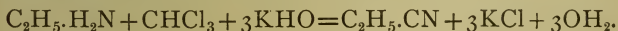
from which the latter may be liberated by distillation with a strong aqueous solution of potassic cyanide :



Also by distilling a dry mixture of potassic cyanide (or ferro-cyanide) with potassic ethylic sulphate (potassic sulphonylate) a mixed product is obtained, but in this case the derivative of higher boiling-point constitutes the major portion :



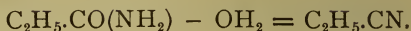
Again, it will be remembered that when trichloromethane acts upon ammonia in presence of potassic hydrate (p. 60), hydrocyanic acid is formed ; if, in place of ammonia, a primary amine (*i.e.* a compound derived from ammonia by the replacement of H by a monad radicle) of the  $\text{C}_n\text{H}_{2n+1}\text{.H}_2\text{N}$  series be taken, a compound is obtained bearing to hydrocyanic acid the same relation that the amine bears to ammonia. Thus, in the case of ethylamine (amidoethane) the following reaction occurs :



The product of this reaction consists wholly of the cyanethane of lower boiling-point.

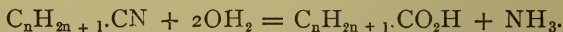
Finally, the cyanethane of higher boiling-point may be obtained in the pure state by distillation of the acid amide

of propionic acid (propionamide) with phosphoric anhydride :

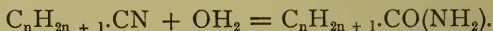


All these methods may be generalised, and thus a homologous series of compounds produced bearing to methane and its homologues the same relations that the two cyano-derivatives of ethane bear to ethane. The derivatives of higher boiling-point are usually termed alcoholic cyanides or nitriles : thus, ethylic cyanide is also called propionitrile, in allusion to its formation from propionic acid ; those of lower boiling-point are known as alcoholic isocyanides or carbamines, on account of their relation to the amines.

The nitriles are ultimately converted on heating with water into the acid of the acetic series containing the same number of units of carbon and ammonia, thus :



An intermediate product may be obtained, however, viz., the acid amide containing the same number of units of carbon :

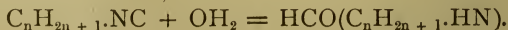


The decomposition is greatly facilitated by the addition either of a mineral acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ), or of an alkali.

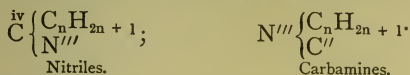
The carbamines are converted by the action of water into formic acid and an amine containing one unit of carbon less than the carbamine :



This reaction takes place slowly when pure water, or an alkaline solution, is employed, but is very rapidly effected in presence of a mineral acid. An intermediate product is also obtained from the carbamines, viz., the substituted acid amide of formic acid :



In virtue of these decompositions, the two classes of cyanides are represented by the following rational formulæ :



Hence, according to the definition given on p. 29, the two series are metameric.<sup>1</sup>

The carbamines possess pungent, nauseous odours, and are highly poisonous ; they invariably boil at lower temperatures than the nitriles, and their chemical activity is also far greater : thus, they combine immediately, with great evolution of heat, with the haloid acids and the inorganic oxacids ; they combine readily with the moniodo-derivatives of the paraffins ; they react most violently with argentic and mercuric oxide, and are converted into cyanates (carbimides) :  $\text{C}_n \text{H}_{2n+1} . \text{NC} + \text{HgO} = \text{C}_n \text{H}_{2n+1} . \text{NCO} + \text{Hg}$ . The nitriles, on the other hand, apparently are not poisonous, and their odours are not unpleasant ; they unite far less readily than the carbamines with the haloid acids, and not at all with the inorganic oxacids or moniodo-paraffins ; and they are not oxidised on treatment with  $\text{Ag}_2\text{O}$  or  $\text{HgO}$ . The carbamines undergo change when heated in closed vessels above their boiling-points, but the nature of the products has not yet been satisfactorily ascertained ; there is little doubt, however, that a portion of the carbamine is converted into the corresponding nitrile.

### $\text{C}_n \text{H}_{2n}$ OR OLEFINE SERIES OF HYDROCARBONS.

The same general relations exist among the members of this series as among the paraffins. The chemical be-

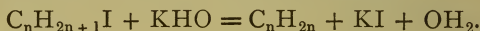
<sup>1</sup> Each of these metameric series, however, includes isomerides ; thus, for example, the  $\alpha$ -cyanopropane ( $\alpha$ -propionitrile) and  $\alpha$ -isocyanopropane ( $\alpha$ -propylic carbamine) obtained by the agency of  $\alpha$ -iodopropane (propylic iodide),  $\text{C}_3\text{H}_7\text{I}$ , are isomeric respectively with the  $\beta$ -cyanopropane and  $\beta$ -isocyanopropane yielded by  $\beta$ -iodopropane (isopropylic iodide).



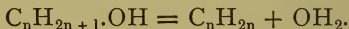
haviour of the first member of the series, ethylene,  $C_2H_4$ , has alone been studied with any considerable degree of thoroughness. The following olefines have been obtained :—

| Name           | Formula     | P. B.          | Name        | Formula        | B. P.            |
|----------------|-------------|----------------|-------------|----------------|------------------|
| Ethylene       | $C_2H_4$    | — <sup>o</sup> | Octylene    | $C_8H_{16}$    | 120 <sup>o</sup> |
| Propylene      | $C_3H_6$    | -18            | Nonylene    | $C_9H_{18}$    | 140              |
| Butylene       | $C_4H_8$    | —              | Diamylene   | $C_{10}H_{20}$ | 160              |
| Isobutylene    | $C_4H_8$    | -6             | Triamylene  | $C_{15}H_{30}$ | 240-250          |
| Pseudobutylene | $C_4H_8$    | 3              | Cetene      | $C_{16}H_{32}$ | 275              |
| Amylene        | $C_5H_{10}$ | —              | Tetramylene | $C_{20}H_{40}$ | 390-400          |
| Hexylene       | $C_6H_{12}$ | 65             | Cerotene    | $C_{27}H_{54}$ | ?                |
| Heptylene      | $C_7H_{14}$ | 96             | Melene      | $C_{30}H_{60}$ | 375 (?)          |

*General Methods of Preparation.*—1. By the action of potassic hydrate in aqueous or alcoholic solution on the mono-haloid derivatives of the paraffins, e.g. :



2. By the abstraction of the elements of water from the monohydric alcohols of the  $C_nH_{2n+1}.OH$  series of alcohols, by the action of sulphuric acid, phosphoric anhydride, or zinc chloride :



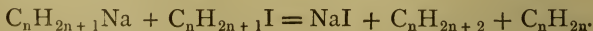
3. By the electrolysis of the acids of the  $C_nH_{2n}(CO_2H)_2$  series :



4. By the action of sodium on a mixture of a moniodo-paraffin with a moniodo-olefine :



5. By the action of the sodium organo-metallic compounds of the  $C_nH_{2n+1}Na$  series on the moniodo-paraffins :

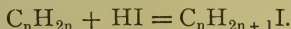


6. By the action of heat on the organic analogues of ammoniac hydrate, of the general formula  $N(C_nH_{2n+1})_4.OH$ :

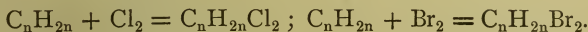


and in many cases of destructive distillation.

*General Reactions.*—1. The olefines unite directly with the haloid acids (most readily with hydriodic acid), forming mono-haloid substitution-derivatives of the paraffins, e.g. :



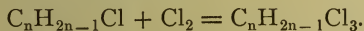
2. All olefines combine directly with chlorine and bromine, some with iodine ; and also with iodine and bromine chlorides,  $ICl$  and  $BrCl$ , and give rise to the formation of di-haloid substitution derivatives of the paraffins, e.g. :



These di-derivatives may be converted into mono-haloid substitution-derivatives of the olefines by the action of an alcoholic solution of potassic hydrate, thus :



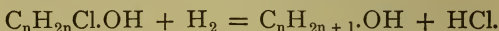
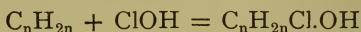
The mono-substituted olefines so produced combine directly with chlorine or bromine to form trichlorinated, or tribrominated paraffins, from which dichlorinated, or dibrominated olefines may be obtained by treatment with potassic hydrate, e.g. :



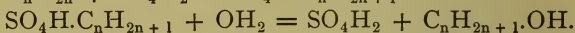
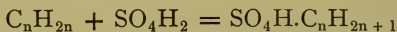
By repeating these two operations olefines may be produced in which the whole of the hydrogen is replaced by chlorine or bromine ; these compounds also combine directly with chlorine or bromine, forming 'per-substituted' paraffins. In this manner, for example, the following series of brominated derivatives have been obtained from ethylene :—

|                                                                 |              |
|-----------------------------------------------------------------|--------------|
| Ethylene . . . . .                                              | $C_2H_4$     |
| Bromethylene . . . . .                                          | $C_2H_3Br$   |
| Dibromethylene . . . . .                                        | $C_2H_2Br_2$ |
| Tribromethylene . . . . .                                       | $C_2HBr_3$   |
| Tetrabromethylene . . . . .                                     | $C_2Br_4$    |
| Ethylene dibromide ( $\alpha$ -Dibromethane) . . . . .          | $C_2H_4Br_2$ |
| Bromethylene dibromide ( $\alpha$ -Tribromethane) . . . . .     | $C_2H_3Br_3$ |
| Dibromethylene dibromide ( $\alpha$ -Tetrabromethane) . . . . . | $C_2H_2Br_4$ |
| Tribromethylene dibromide (Pentabromethane) . . . . .           | $C_2HBr_5$   |
| Tetrabromethylene dibromide (Hexabromethane) . . . . .          | $C_2Br_6$    |

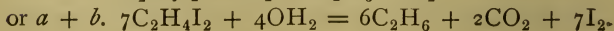
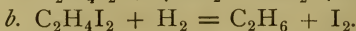
3. The olefines combine with hypochlorous acid, forming monochlorinated monohydric alcohols, convertible into the corresponding alcohols by the action of nascent hydrogen :



4. The olefines also unite directly with sulphuric acid to form 'acid ethereal salts'; these are converted, on distillation with water, into sulphuric acid and the monohydric alcohol containing the same number of unit-weights of carbon as the olefine :



The olefines do not combine directly with nascent hydrogen under ordinary conditions to reproduce the corresponding paraffins, but by heating ethylene iodide (diiodethane) with water in hermetically closed tubes for some hours at  $275^\circ$ , it is partially converted into ethane. The formation of ethane is in this case due to the action of the hydrogen set free by the decomposition of a portion of the diiodethane, on the remaining portion of the latter, as expressed by the following equations :—



ETHYLENE (*Ethene*),  $C_2H_4$ .—*Preparation*.—1. By the action of nascent hydrogen on acetylene :



Acetylene is the only hydrocarbon which can be obtained by the direct union of its elements ; and since ethylene may be readily converted into ordinary alcohol (see 4th general reaction), peculiar interest attaches to this mode of formation of ethylene, as it is thus possible, by a connected series of simple reactions, to build up alcohol from its constituent elements, carbon, hydrogen, and oxygen.

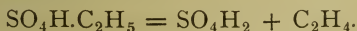
2. Ethylene may be obtained by all of the above general methods, but is best prepared by the action of sulphuric acid on alcohol at a temperature of about  $165^\circ$  :—

A mixture of three parts of water and ten parts of concentrated sulphuric acid is heated in a flask to about  $160^\circ$ – $165^\circ$  ; ordinary alcohol is then slowly dropped in, and the evolved gas passed through wash-bottles containing respectively sodic hydrate solution and concentrated sulphuric acid ; in the first it is freed from carbonic and sulphurous anhydrides, in the second from ether, alcohol, and water vapour carried over mechanically.

The first reaction in this process consists in the formation of hydric ethylic sulphate (*sulphovinic acid*), as expressed by the equation :



but at the temperature to which the mixture is heated this is a highly unstable compound, and is rapidly resolved into ethylene and sulphuric acid :



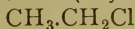
If the temperature be so adjusted that the amount of water distilling over with the gas is about equal to the amount of water formed in the reaction, a relatively small quantity of acid suffices to convert a very considerable quantity of alcohol into ethylene and water.

*Properties.*—Ethylene is a colourless, odourless gas, but is condensable, under the combined influence of pressure and extreme cold, to a liquid. It is almost insoluble in water. It burns with a bright white flame. Ethylene is decomposed into carbon and methane by passing through a red-hot tube:  $C_2H_4 = CH_4 + C$ ; at a somewhat lower temperature, acetylene ( $C_2H_2$ ) and hydrogen are the products.

*α-Dichlorethane (Ethylene Chloride; Dutch Liquid)*,  $C_2H_4Cl_2$ . Ethylene and chlorine combine directly and with moderate rapidity in diffused daylight in the proportion of equal volumes. If the mixture be exposed to bright sunlight, substitution-derivatives of *α*-dichlorethane are also produced. Ethylene chloride is a colourless liquid of agreeable ethereal odour; sp. gr. 1.256 at 12°. It boils at 84° and is isomeric with the *β*-dichlorethane obtained by the action of chlorine on monochlorethane (ethylic chloride); this modification, which is commonly known as ethylidene chloride, boils at 60°; its sp. gr. is 1.174 at 17°. Both, however, yield the same monochlorethylene (vinyl chloride),  $C_2H_3Cl$ , on treatment with an alcoholic solution of potassic hydrate. Monochlorethylene is gaseous at ordinary temperatures, but may be condensed to a liquid, which boils at -18°; it combines with chlorine forming *α*-trichlorethane.

The mono- and di-derivative obtained by the action of chlorine on ethylene chloride are respectively isomeric with the mono- and di-chlorinated derivative of ethylidene chloride, but identical penta- and hexa-chlorethanes are obtained from ethylene and ethylidene chlorides. The following list comprises the known chlorinated derivatives of ethane:—

Monochlorethane (Ethylic chloride).



B.P. 12.5°.

*α*-Dichlorethane  
(Ethylene chloride).



B.P. 84°; S.G. 1.256 at 12°.

*β*-Dichlorethane  
(Ethylidene chloride).



B.P. 57.5°; S.G. 1.174 at 17°.

$\alpha$ -Trichlorethane  
 $\text{CH}_2\text{Cl}.\text{CHCl}_2$

B.P.  $115^\circ$ ; S.G. 1.422 at  $17^\circ$ .

$\alpha$ -Tetrachlorethane.  
 $\text{CHCl}_2.\text{CHCl}_2$

B.P.  $147^\circ$ ; S.G. 1.614 at  $0^\circ$ .

Pentachlorethane.  
 $\text{CHCl}_2.\text{CCl}_3$

B.P.  $158^\circ$ .

$\beta$ -Trichlorethane.  
 $\text{CH}_3.\text{CCl}_3$

B.P.  $75^\circ$ ; S.G. 1.372 at  $0^\circ$ .

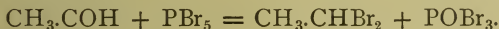
$\beta$ -Tetrachlorethane.  
 $\text{CH}_2\text{Cl}.\text{CCl}_3$

B.P.  $127.5^\circ$ ; S.G. ?

Hexachlorethane.  
 $\text{CCl}_3.\text{CCl}_3$

Melts at  $226^\circ$ ; B.P.  $331^\circ$ .

$\alpha$ -Dibromethane (*Ethylene Bromide*),  $\text{C}_2\text{H}_4\text{Br}_2$ .—On passing ethylene into liquid bromine it is at once absorbed, with considerable evolution of heat. Pure  $\alpha$ -dibromethane thus prepared is a colourless liquid of ethereal odour, boiling at  $129^\circ$ ; treatment with an alcoholic solution of potassic hydrate converts it into bromethylene,  $\text{C}_2\text{H}_3\text{Br}$ , which is gaseous at ordinary temperatures, but is readily condensed by a refrigerating mixture of ice and salt to a colourless liquid.  $\beta$ -Dibromethane (*Ethylidene Bromide*), which boils at  $110^\circ$ – $112^\circ$ , is obtained by heating monobromethane with bromine, or by treatment of aldehyde with phosphorus pentabromide :



Both monochlor- and monobrom-ethylene undergo a remarkable spontaneous change when preserved in the liquid state, and are converted into white, solid, amorphous polymerides.

*Diiodethane (Ethylene Iodide)*,  $\text{C}_2\text{H}_4\text{I}_2$ , is obtained on passing ethylene into a pasty mixture of iodine with absolute alcohol. It is a white crystalline substance.

PROPYLENE (*Propene*),  $\text{C}_3\text{H}_6$ , may be obtained by the action of an alcoholic solution of potassic hydrate on isopropyl iodide ( $\beta$ -iodopropane), or by distilling isopropyl alcohol with zinc chloride; it is best prepared by the action of nascent hydrogen on allylic iodide,  $\text{C}_3\text{H}_5\text{I}$ . Propylene is a gas like ethylene.



Ethylene is represented by the formula  $\text{H}_2\text{C}=\text{CH}_2$ , and all the homologous hydrocarbons may be regarded as derived from it by the substitution of hydrocarbon radicles of the form  $\text{C}_n\text{H}_{2n+1}$  for one or more of its hydrogen atoms. Thus, propylene,  $\text{C}_3\text{H}_6$ , is methylethylene  $\text{H}_2\text{C}=\text{CH}.\text{CH}_3$ , and only one methylethylene is possible ; but butylene may exist in three isomeric modifications, viz. :

- |                               |   |   |                                                       |
|-------------------------------|---|---|-------------------------------------------------------|
| 1. Ethylethylene              | . | . | $\text{H}_2\text{C}=\text{CH}.\text{C}_2\text{H}_5$ . |
| 2. $\alpha$ -Dimethylethylene | . | . | $\text{CH}_3.\text{HC}=\text{CH}.\text{CH}_3$ .       |
| 3. $\beta$ -Dimethylethylene  | . | . | $\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$ .        |

These are all known, 1. being obtained from normal primary butylic iodide,  $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_2\text{I}$  ; 2. from secondary butylic iodide,  $\text{CH}_3.\text{CH}_2.\text{CHI}.\text{CH}_3$  ; and 3. from both isopropyl and tertiary butylic iodides,  $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{I}$  and  $\text{C}(\text{CH}_3)_3\text{I}$ , by the first general method of preparation.

Recent investigations appear to have established the following 'laws' with regard to the olefines : 1. That in their formation by the first and second general methods, when the halogen of the haloid derivative, or the hydroxyl group of the alcohol, is withdrawn together with an atom of hydrogen, the negative radicle and the hydrogen thus withdrawn are always derived from carbon atoms contiguous in the formula ; it will be obvious that this is the case on comparing the formulæ of the butylic iodides with those of the corresponding butylenes. 2. That there is a tendency to the production of those modifications which contain a maximum number of methyl groups ; secondary butylic iodide, for example, yields dimethylethylene and not ethylethylene. 3. That whenever the olefines combine with other compounds of the general form  $\text{X}'\text{Y}'$ ,  $\text{X}'$  being the positive and  $\text{Y}'$  the negative radicle of the compound, there is a tendency for the negative radicle to combine with that carbon atom which the formula of the olefine shows to be least hydrogenised ; thus propylene and sulphuric acid form isopropylic and not normal propylic hydrogen sulphate.

$C_nH_{2n-2}$  OR ACETYLENE SERIES OF HYDROCARBONS.

The following are members of this group :—

|                 |   |   |   |   |   |                |
|-----------------|---|---|---|---|---|----------------|
| Acetylene       | . | . | . | . | . | $C_2H_2$       |
| Allylene        | . | . | . | . | . | $C_3H_4$       |
| Crotonylene     | . | . | . | . | . | $C_4H_6$       |
| Valerylene      | . | . | . | . | . | $C_5H_8$       |
| Propylacetylene | . | . | . | . | . | $C_5H_8$       |
| Diallyl         | . | . | . | . | . | $C_6H_{10}$    |
| Rutylene        | . | . | . | . | . | $C_{10}H_{18}$ |

Isomeric modifications of several of these are known.

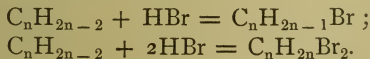
*Preparation.*—Two general methods are employed. The first of these consists in acting upon a mono-haloid derivative of an olefine with an alcoholic solution of potassic hydrate :



The second method of preparation is the electrolysis of the acids of the  $C_nH_{2n-2}(CO_2H)_2$ , or maleic series :



*General Reactions.*—The hydrocarbons of the acetylene series all combine directly with the halogens, and yield with bromine, for example, either saturated compounds of the form  $C_nH_{2n-2}Br_4$  (tetra-brominated paraffins), or intermediate compounds of the form  $C_nH_{2n-2}Br_2$  (di-brominated olefines). They also unite directly in two proportions with the haloid acids, to form either mono-substituted olefines, or di-substituted paraffins, e.g. :



Especially characteristic of many of the hydrocarbons of this series is the formation of metallic substitution-derivatives ; thus if acetylene be passed into an ammoniacal solution of cuprous chloride, a red-brown precipitate, said to have the

composition  $C_4H_2Cu_2 + Cu_2O$ ,<sup>1</sup> is obtained; the corresponding argentic compound is produced if an ammoniacal solution of argentic nitrate be employed. All the members of the series do not yield such products, however; thus several isomeric allylenes are known (see citraconic acid), one of which yields a white crystalline argentic derivative,  $C_3H_3Ag$ , and corresponding copper and mercury compounds, but the others are incapable of furnishing metallic derivatives. These derivatives are readily decomposed by hydrochloric acid, with re-formation of the hydrocarbon and metallic chloride.

ACETYLENE,  $C_2H_2$ . *Preparation*.—1. The direct formation of acetylene from its elements may be effected by passing hydrogen over intensely-heated carbon. The electric arc from a powerful voltaic battery is caused to pass between poles of hard carbon arranged in a glass globe, through which a current of hydrogen is transmitted, and the issuing gas is washed by an ammoniacal solution of cuprous chloride. By no other means is it possible to raise the temperature of the carbon sufficiently high to effect the combination.

2. By the action of an alcoholic solution of potassic hydrate on bromethylene,  $C_2H_3Br$ .

3. By the electrolysis of fumaric and maleic acids:



4. By passing a mixture of methane and carbonic oxide through a red-hot tube:  $CH_4 + CO = C_2H_2 + OH_2$ .

5. By passing trichloromethane vapour over ignited copper:  $2CHCl_3 + 6Cu = 3Cu_2Cl_2 + C_2H_2$ .

6. By passing induction-sparks through methane; by the action of heat on ethylene, or the vapours of alcohol, ether, &c.; by the incomplete combustion of bodies containing carbon and hydrogen; in fact, acetylene is a constant pro-

<sup>1</sup> According to Blochmann (*Liebig's Annalen*, clxxiii. 176), the composition of cuprous acetylide dried over calcic chloride is represented by the formula  $C_2H_2Cu_2O$ , and that of the corresponding silver compound by the formula  $C_2H_2Ag_2O$ .

duct of the decomposition by heat, or incomplete combustion, of most organic compounds.

To purify the crude acetylene obtained by any of these methods it is passed into an ammoniacal solution of cuprous chloride, whereby the characteristic red precipitate of cuprous acetylide is produced ; the liquid containing the precipitate is next heated to boiling, in order to decompose a derivative which ethylene forms with copper, and the precipitate is then collected on a filter, washed, and dried over sulphuric acid in vacuo. Cuprous acetylide explodes readily by percussion, and also when heated slightly below  $100^{\circ}$  ; on boiling it with hydrochloric acid pure acetylene is evolved.

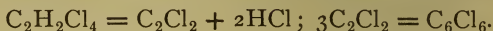
Acetylene is a colourless, incondensable gas, moderately soluble in water ; it possesses a peculiar, unpleasant, highly characteristic odour, and burns with a luminous smoky flame.

By the action of nascent hydrogen on cuprous acetylide ethylene is obtained. For this purpose the acetylide is mixed with zinc and dilute ammonia solution, and the mixture gently warmed. The hydrogen liberated by the action of the zinc on the ammonia, acting upon the copper compound, sets free acetylene, which, it may be supposed, at the moment of liberation unites with the nascent hydrogen to form ethylene.

Acetylene unites with bromine to form acetylene dibromide (dibromethylene),  $C_2H_2Br_2$ , and acetylene tetrabromide (tetrabromethane),  $C_2H_2Br_4$ . The action of chlorine on acetylene is so violent that explosion with separation of carbon usually ensues on mixing the gases ; by the action of antimonious pentachloride, however, the two compounds,  $C_2H_2Cl_2$  (acetylene dichloride, dichlorethylene), and  $C_2H_2Cl_4$  (acetylene tetrachloride,  $\alpha$ -tetrachlorethane) are obtained.

When passed through a red-hot tube, acetylene is partly converted into *benzene* :  $3C_2H_2 = C_6H_6$ . At the same time a number of higher condensation-products are obtained. Similarly, by heating acetylene tetrachloride with water to  $360^{\circ}$ , *hexachlorobenzene* is formed. In this case, probably

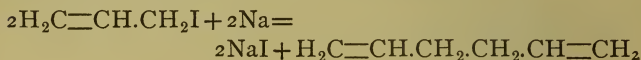
the chloride is first resolved into hydrochloric acid and dichloroacetylene, which at once undergoes condensation:



Acetylene may be regarded as having the constitution represented by the formula



Homologous hydrocarbons may be derived from it by substituting radicles of the form  $\text{C}_n\text{H}_{2n+1}$  for the half or the whole of its hydrogen; but only those represented by the general formula  $\text{HC}\equiv\text{C.C}_n\text{H}_{2n+1}$  are capable of furnishing metallic derivatives. Thus the next homologue of acetylene,  $\text{C}_3\text{H}_4$ , exists in two isomeric modifications: one of these, known as *allylene*, is for various reasons represented by the formula  $\text{HC}\equiv\text{C.CH}_3$ , and is capable of forming metallic derivatives; but the other, known as *allene*, has not this property, and in all probability is represented by the formula  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ . Again, *diallyl*,  $\text{C}_6\text{H}_{10}$ , which is obtained by acting on allylic iodide with sodium, and therefore does not contain the group  $\text{HC}\equiv$  in its formula



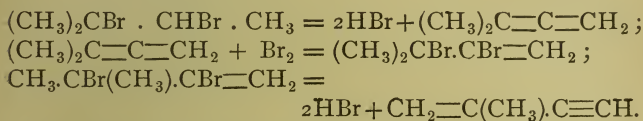
is also incapable of forming metallic derivatives.

#### $\text{C}_n\text{H}_{2n-4}$ SERIES OF HYDROCARBONS.

Very few members of this series have been produced artificially, but it includes the hydrocarbons of the formula  $\text{C}_{10}\text{H}_{16}$ , which occur so frequently in various plants.

VALYLENE,  $\text{C}_5\text{H}_6$ , the lowest known term of the series, is obtained by acting with an alcoholic solution of potassic hydrate on the dibromide of the hydrocarbon valerylene,  $\text{C}_5\text{H}_8$ , derived from amylene,  $\text{C}_5\text{H}_{10}$ , from fermentation amylic alcohol. This amylene, however, is a mixture of three, if not four, isomeric hydrocarbons, but consists prin-

cipally of trimethylethylene,  $(\text{CH}_3)_2\text{C}=\text{CH}.\text{CH}_3$ . Valylene boils at about  $60^\circ$ ; it combines with bromine, forming a crystalline *hexabromide*,  $\text{C}_5\text{H}_6\text{Br}_6$ ; and when mixed with an ammoniacal solution of cuprous chloride, it yields a precipitate of the composition  $(\text{C}_5\text{H}_5)_2\text{Cu}_2$ , from which the hydrocarbon is again obtained on treatment with hydrochloric acid. This last-mentioned property is an indication that the hydrocarbon contains the group  $\text{HC}\equiv$  in its formula, and supposing that it is derived from trimethylethylene, its formation from the dibromide of this olefine may be represented by the following equations :



TERPENES AND CITRENES.—A very large number of plants furnish more or less *essential oil* when their leaves or other parts are distilled with water. Usually these essential oils consist chiefly of hydrocarbons of the formula  $\text{C}_{10}\text{H}_{16}$ ; oxidised bodies, such as are represented by the formulæ  $\text{C}_{10}\text{H}_{16}\text{O}$ ,  $\text{C}_{10}\text{H}_{18}\text{O}$ , and  $\text{C}_{10}\text{H}_{20}\text{O}$ , are also contained in most of them, and these are doubtless closely related to the hydrocarbons with which they are associated, although the nature of the relation is as yet unknown.

The oils are in some cases extracted by mere pressure, as oil of lemons from the rind of the fruit, but more often they are obtained, as before said, by distilling the leaves or other parts with water, the oil being then carried over mechanically and condensed with the steam. Ordinary *oil of turpentine* is obtained from so-called *turpentine*, the oleo-resinous juice which exudes from excisions made in the stems of pines, firs, and other coniferæ, by distillation either alone or with water; the portion which does not distil constitutes ordinary *rosin* or *colophony*, and consists of an oxidised body probably of the formula  $\text{C}_{44}\text{H}_{62}\text{O}_4$ . The oil of turpentine



chiefly used in this country is obtained from the turpentine collected in the Southern States of America from *Pinus australis*, *P. Tæda*, and other conifers. French oil of turpentine is extracted from the turpentine furnished by the *Pinus maritima*, which is largely cultivated in Southern France, in the neighbourhood of Bordeaux. Russian and Swedish oil of turpentine are from *Pinus sylvestris*.

Most essential oils are colourless when pure—those of chamomile and wormseed are said to be blue—and usually possess a pronounced characteristic odour, which, however, is probably due to the oxidised constituent. They mix in all proportions with fat oils, and also dissolve in alcohol and ether.

The hydrocarbons of the formula  $C_{10}H_{16}$  derived from plants may be divided into two classes, viz.: (1) those boiling at about  $156^{\circ}$ , which are conveniently termed *terpenes*, as they are the chief constituents of the ordinary turpentine oils; and (2) those boiling at about  $176^{\circ}$ – $178^{\circ}$ , which may be termed *citrenes*, as they are the chief constituents of the oils derived from the various species of *Citrus*. The terpenes and citrenes are all capable of deviating, or, as it is termed, rotating the plane of polarisation of a ray of light, but no two plants furnish terpenes or citrenes of identical rotatory power, and often different parts of the same plant yield different products; the different terpenes appear, however, to agree in all other physical properties and also in their chemical properties, and the same is true of the different citrenes. It is probable that the number of isomerides of the formula  $C_{10}H_{16}$  is very much smaller than has been supposed, and that the differences observed in the rotatory powers of the hydrocarbons from various sources are due to their being mixtures in varying proportions of two or more isomerides.

The terpenes undergo isomeric change with remarkable facility, and apparently very few, if any, of the compounds which they furnish are directly derived from them. They

readily combine with hydrochloric acid, but the nature of the product depends on the conditions observed. If saturated with the gas, they are almost entirely converted into a solid crystalline *monohydrochloride*,  $C_{10}H_{17}Cl$ , the monohydrochlorides obtained from the different terpenes being distinguishable only by their behaviour in polarised light. But if placed in contact with the aqueous acid, or if dissolved in alcohol and then submitted to the action of the gas, they yield a crystalline optically inactive *dihydrochloride*,  $C_{10}H_{18}Cl_2$ . The citrenes apparently do not under any circumstances form a solid monohydrochloride, but are at once converted into dihydrochloride when saturated with the gas. With one exception, they all furnish the same dihydrochloride, which moreover is not distinguishable from that prepared from the terpenes; the exception referred to is *sylvestrene*, one of the constituents of the oil of turpentine from *Pinus sylvestris*, which yields a dihydrochloride melting at  $72^\circ$ , whereas that prepared from all other citrenes and terpenes melts at about  $50^\circ$ .

Bromine acts with great violence on the terpenes and citrenes, much heat being developed by the union of the two bodies. If they are carefully brought together with bromine at a low temperature, they form *tetrabromides* of the formula  $C_{10}H_{16}Br_4$ , but they cannot be united with a larger proportion of this halogen. Their dibromides readily decompose on distillation, with evolution of hydrobromic acid and production of *cymene* or *paramethylpropylbenzene*,  $C_{10}H_{14}=C_6H_4(CH_3)(C_3H_7)^a$ ; the different hydrocarbons, however, yield very different amounts of cymene, a much larger quantity being formed by the decomposition of the citrene dibromides than is obtained by the decomposition of the terpene dibromides; the dibromide of the citrene which is the chief constituent of oil of orange yields as much as 80 per cent. of cymene. Many essential oils contain small quantities of cymene.

When left for some time in contact with an alcoholic solution

of nitric, hydrochloric or sulphuric acid, the terpenes assimilate the elements of water and form a crystalline optically inactive compound of the formula  $C_{10}H_{20}O_2 + OH_2$ , commonly known as *terpin*, but which is more appropriately termed *terpilenol*, as it belongs to the class of compounds known as alcohols, its rational formula being  $C_{10}H_{18}(OH)_2$ . Terpilenol has also been obtained from some of the citrenes, the citrene from lemon oil being very readily converted into it. When submitted to the action of hydrochloric acid, terpilenol yields a dihydrochloride identical with that obtained by combining the terpenes and citrenes with hydrochloric acid.

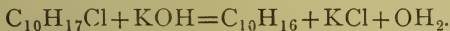
The terpenes and citrenes are very readily oxidised, and apparently all yield the same products. If a mixture of potassic dichromate and sulphuric acid is employed as oxidising agent, *diaterpenylic acid*, a dibasic acid of the formula  $C_8H_{14}O_5$ , is produced, but this acid at once breaks up into water and *terpenylic acid*,  $C_8H_{12}O_4$ . If nitric acid is used, *diaterebic acid*,  $(CH_3)_2CH \cdot CH(OH) \cdot CH(COOH)_2$ , is formed, which also breaks up in a similar manner into water and *terebic acid*,  $C_7H_{10}O_4$ . On exposure to moist air they slowly absorb oxygen, and assume the character of resins; their oxidation under these circumstances is attended with the production of hydric peroxide in small quantity.

*Terpilene*. — The dihydrochloride  $C_{10}H_{18}Cl_2$ , prepared from the terpenes and citrenes, is a compound of low stability, and on mere distillation breaks up into hydrochloric acid and *terpilene*, which is also a hydrocarbon of the formula  $C_{10}H_{16}$ . Terpilene is also obtained by warming terpilenol with a mixture of equal volumes of sulphuric acid and water. It boils at the same temperature as the citrenes, and forms the same dihydrochloride, but it is optically inactive, and on exposure to moist air absorbs oxygen much more rapidly than the natural terpenes or citrenes.

*Isoprene*,  $C_5H_8$ , a hydrocarbon of the acetylene series obtained by distilling caoutchouc, and the valerylene pre-

pared from crude amylene (p. 104), are polymerised when heated in closed vessels for several hours at about 250°–260°, and among other products they yield a hydrocarbon which appears to be identical with terpine.

*Camphenes*.—The solid monohydrochlorides prepared from the terpenes are bodies of considerable stability, being scarcely altered by distillation or by heating with water at 100°; but by prolonged heating with an alcoholic solution of potassic hydrate at about 180°, they are decomposed in accordance with the equation :



The camphenes, as the hydrocarbons thus produced are termed, possess very different properties from those of the parent terpenes. They are solid crystalline bodies, and form only monohydrochlorides whatever the conditions under which they are submitted to the action of hydrochloric acid; these monohydrochlorides moreover are very readily decomposed, even by heating with water at 100°, camphene being regenerated. On oxidation with potassic dichromate and sulphuric acid, the camphenes are converted into camphor,  $\text{C}_{10}\text{H}_{16}\text{O}$ . The camphenes prepared in the manner described are optically active, those obtained from dextrorotatory hydrochlorides being dextrorotatory, and those from lævorotatory hydrochlorides lævorotatory.

If the terpenes are treated with concentrated sulphuric acid, much heat is developed, and their optical activity is gradually destroyed. The optically inactive product finally obtained is a mixture of inactive camphene, terpine, and cymene with hydrocarbons polymeric with the terpene. The citrenes appear only to yield terpine, cymene, and polymeric hydrocarbons when similarly treated.

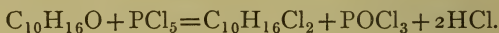
At present we are totally ignorant of the rational formulæ of the terpenes and citrenes. It has been suggested that they are dihydrides of cymene, since this hydrocarbon is obtained by the decomposition of their dibromides; but a

large number of facts, and especially their behaviour on oxidation, entirely negative this hypothesis.

*Oxidised constituents of Essential Oils. Camphors.*—As already remarked, the nature of the relation in which these compounds stand to the hydrocarbons with which they are associated is unknown ; a brief reference to one or two of the more important will therefore suffice.

The best known representative of the  $C_{10}H_{16}O$  group is ordinary *camphor*, a crystalline body obtained from *Laurus camphora* and certain other plants, in which it exists ready formed. This camphor is dextrorotatory. A second modification which has a precisely equal action, but in the opposite direction, on the polarised ray, is present in the oil of feverfew (*Matricaria parthenium*) ; and the oils of lavender, rosemary and sage are said to contain an optically inactive camphor. Only laurel camphor has been investigated, however. As before stated, camphor may be artificially prepared by oxidising the camphenes ; the camphor thus produced is dextro- or lævo-rotatory or inactive according as the camphene is dextro- or lævo-rotatory or inactive.

When submitted to the action of pentachloride of phosphorus, camphor exchanges its oxygen for chlorine :



The compound  $C_{10}H_{16}Cl_2$  decomposes on distillation into cymene,  $C_{10}H_{14}$ , and hydrochloric acid ; by the action of sodium it may be deprived only of its chlorine and converted into camphene,  $C_{10}H_{16}$ , closely resembling if not identical with that obtained from the terpene monohydrochlorides.

Camphor yields a variety of products on oxidation with nitric acid, chief among which is *camphoric acid*, a dibasic acid of the formula  $C_8H_{14}(COOH)_2$ . The camphoric acid obtained by oxidising artificially prepared camphor has a higher melting point ( $203^\circ$ ) than that produced from natural camphor ( $187^\circ$ ). When oxidised by boiling with a mixture

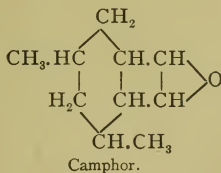
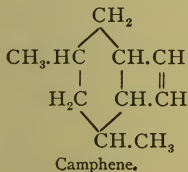


of potassic dichromate and sulphuric acid, camphor yields a small quantity of *adipic acid*,  $C_4H_8(COOH)_2$ , one of the acids of the succinic series.

*Camphol*.—The most important member of the  $C_{10}H_{18}O$  group is *camphol* or *borneol*, a crystalline substance found in cavities in the bark of *Dryobalanops Camphora*, a tree indigenous to Borneo and Sumatra. On oxidation with nitric acid, it is converted into camphor identical in all respects with natural camphor. When acted upon by hydrochloric acid or phosphoric pentachloride, it yields the compound  $C_{10}H_{17}Cl$ . These reactions show that camphol is an alcohol of the formula  $C_{10}H_{17}.OH$ .

If a solution of camphor in toluene is heated with sodium, sodium camphor,  $C_{10}H_{15}NaO$ , is produced; the hydrogen displaced by the sodium is not evolved, however, but acts on a portion of the camphor, converting it into camphol.

The formulæ of camphenes and camphor are not yet satisfactorily established, but the following may be provisionally suggested as not improbable:



### $C_nH_{2n-6}$ OR BENZENE SERIES OF HYDROCARBONS.

These hydrocarbons differ greatly in chemical behaviour from the series previously considered: whereas the members of the  $C_nH_{2n}$ ,  $C_nH_{2n-2}$  and  $C_nH_{2n-4}$  series all tend, as has been shown, to form additive compounds, and are not directly convertible into substitution-derivatives, the members of the benzene series comport themselves in the majority of cases as saturated hydrocarbons, and as a rule yield substitution-derivatives, additive compounds



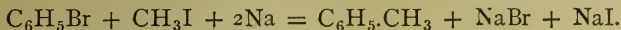
being formed from them only under certain peculiar conditions. They are, moreover, characterised by their extreme stability, and by the multitude of well-marked substitution-derivatives to which they give rise. They are often termed aromatic hydrocarbons, on account of the aromatic odour which some of their derivatives—benzoic acid, for example—possess. The series has been particularly well investigated, and is especially interesting to the chemist, owing to the numerous instances of isomerism which it affords.

The hydrocarbons of the benzene series occur, in small quantity, in petroleum oil, together with the paraffins; but the chief source from which they are obtained is coal-tar oil, one of the products of the destructive distillation of coal as practised in the manufacture of coal gas. The majority have been obtained by synthetic processes.

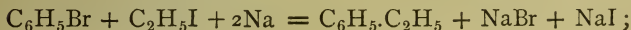
Hitherto no member of the group has been obtained from the corresponding paraffin by a purely chemical and connected series of reactions, in the same manner that olefines or members of the acetylene series have been obtained from the corresponding paraffins, so that we are unable at present to judge whether a hydrocarbon, by composition a member of the  $C_nH_{2n-6}$  series, thus produced, would possess the peculiar properties characteristic of the series exhibited by the members already known.

No hydrocarbon of the series containing less than six unit-weights of carbon has hitherto been discovered. In fact, the first member, *benzene*,  $C_6H_6$ , is to the aromatic series what methane is to the paraffin series, and we may, therefore, conveniently regard the homologues of benzene as derived from it by the substitution of hydrogen by  $C_nH_{2n+1}$  groups, just as the higher paraffins are regarded as formed from methane by the introduction of radicles of the  $C_nH_{2n+1}$  series in place of hydrogen. The system of rational nomenclature adopted in the series is throughout in accordance with this view: thus, *toluene*, the first homologue of benzene, is termed methyl-benzene, because it is obtained

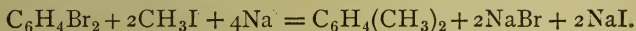
by the action of sodium on a mixture of bromobenzene with iodomethane (methylic iodide) :



The next homologue, *xylene*, of which several modifications exist, is termed ethylbenzene when prepared by the action of sodium on bromobenzene and iodoethane (ethylic iodide) :



and dimethylbenzene when formed by treating dibromobenzene and iodomethane with sodium :



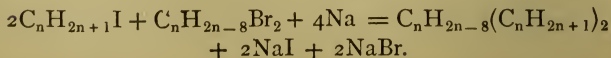
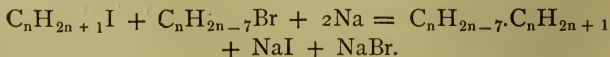
As a matter of fact, no isomerides of toluene, the monomethyl-derivative of benzene, have been discovered. Similarly, only one ethylbenzene is known, but no less than three isomeric modifications of dimethylbenzene have been obtained. In the present state of our knowledge, we are therefore led to assume that isomerism may exist in this series:—  
1. Between compounds which may be regarded as containing the same groups, as in the case of the three isomeric dimethylbenzenes ; 2. between compounds containing isomeric modifications of the same group, as between propyl- and isopropylbenzene ; and 3. between compounds into whose constitution different groups may be assumed to enter, as examples of which ethylbenzene and dimethylbenzene may be cited. Strictly speaking, according to the definition given on page 29, the compounds included in this third division are meta-meric, and not isomeric.

Conformably to this view, the nature of the hydrocarbons of the series may be inferred in two ways :—1. By preparing them synthetically ; 2. by noting their behaviour on oxidation.

The following is a list of most of the known hydrocarbons of the  $\text{C}_n\text{H}_{2n-6}$  series, together with their boiling-points :

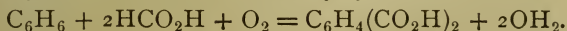
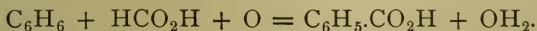
|                |                                                |                                   |              |
|----------------|------------------------------------------------|-----------------------------------|--------------|
| $C_6H_6$       | Benzene . . . .                                | $C_6H_6$                          | B. P.<br>81° |
| $C_7H_8$       | Methylbenzene (toluene) .                      | $C_6H_5(CH_3)$                    | 111          |
| $C_8H_{10}$    | Ethylbenzene . . . .                           | $C_6H_5(C_2H_5)$                  | 135          |
|                | Dimethylbenzenes :—                            |                                   |              |
|                | Paraxylene . . . .                             | $C_6H_4(CH_3)_2$                  | 136          |
|                | Metaxylene . . . .                             | $C_6H_4(CH_3)_2$                  | 137–138      |
| $C_9H_{12}$    | Orthoxylene . . . .                            | $C_6H_4(CH_3)_2$                  | 140–142      |
|                | Propylbenzene . . . .                          | $C_6H_5(C_3H_7)^\alpha$           | 157          |
|                | Isopropylbenzene . . . .                       | $C_6H_5(C_3H_7)^\beta$            | 151          |
|                | Ethylmethylbenzene . . . .                     | $C_6H_4(CH_3)(C_2H_5)$            | 159–160      |
|                | Trimethylbenzenes :—                           |                                   |              |
| $C_{10}H_{14}$ | Mesitylene . . . .                             | $C_6H_3(CH_3)_3$                  | 163          |
|                | Pseudocumene . . . .                           | $C_6H_3(CH_3)_3$                  | 166          |
|                | Isobutylbenzene . . . .                        | $C_6H_5(C_4H_9)^\beta$            | 159–161      |
|                | Propylmethylbenzene or<br>cymene . . . .       | $C_6H_4(CH_3)(C_3H_7)^\alpha$     | 175–176      |
|                | Isopropylmethylbenzene . . . .                 | $C_6H_4(CH_3)(C_3H_7)^\beta$      | 171–172      |
|                | Diethylbenzene . . . .                         | $C_6H_4(C_2H_5)_2$                | 178–179      |
| $C_{11}H_{16}$ | Ethyl dimethylbenzene . . . .                  | $C_6H_3(C_2H_5)(CH_3)_2$          | 183–184      |
|                | Tetramethylbenzene<br>(durene) . . . .         | $C_6H_2(CH_3)_4$                  | 189–191      |
|                | Isoamylbenzene . . . .                         | $C_6H_5(C_5H_{11})^\beta$         | 193          |
| $C_{12}H_{18}$ | Isopropyldimethylbenzene<br>(laurene?) . . . . | $C_6H_3(CH_3)_2(C_3H_7)^\beta$    | 188          |
|                | Diethylmethylbenzene . . . .                   | $C_6H_3(CH_3)(C_2H_5)_2$          | 178          |
| $C_{12}H_{18}$ | Isoamylmethylbenzene . . . .                   | $C_6H_4(CH_3)(C_5H_{11})^\beta$   | 213          |
| $C_{13}H_{20}$ | Isoamyldimethylbenzene . . . .                 | $C_6H_3(CH_3)_2(C_5H_{11})^\beta$ | 232–233      |

*General Methods of Formation.*—The one general method of ascending the series consists in acting upon a mixture of a moniodated paraffin with a brominated derivative of benzene, or one of the homologous hydrocarbons, with sodium :



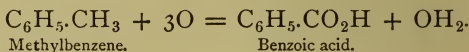
Thus monobromobenzene and iodomethane yield toluene (methylbenzene) ; dibromobenzene, or bromotoluene, and iodomethane yield xylene (dimethylbenzene) ; bromodimethylbenzene and iodomethane yield trimethylbenzene ; bromotrimethylbenzene and iodomethane yield tetramethylbenzene. Penta- and hexamethylbenzenes have not thus been synthesised. If instead of bromobenzene and iodomethane, bromobenzene and iodethane, iodopropane, or iodotetrane are acted upon by sodium, so-called ethyl-, propyl-, or butylbenzenes are obtained. Similarly, bromotoluene, iodethane and sodium yield ethylmethylbenzene ; so that a great variety of compounds may be prepared in this way. The isobutyl- and isoamyl-derivatives included in the above table have all been prepared with the aid of  $\beta$ -iodotetrane and  $\beta$ -iodopentane, obtained from fermentation butylic and amylic alcohol respectively.  $\beta$ -iodopropane cannot be employed in the preparation of  $\beta$ - (so-called iso) propyl-derivatives, which are either natural products, or are obtained by indirect methods.

*Behaviour on Oxidation.*—The first member of the series, benzene, is either unaffected by oxidising agents or is entirely burnt to carbonic anhydride and water ; under no conditions hitherto discovered does it yield oxidation products containing the same number of unit-weights of carbon as itself. It may be directly converted, however, under the influence of certain oxidising agents, into benzoic ( $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H}$ ) and phthalic ( $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ ) acids ; this change occurs when benzene is acted upon by a mixture of manganic oxide ( $\text{MnO}_2$ ) and sulphuric acid, in which case a portion of the benzene is undoubtedly oxidised to formic acid ( $\text{HCO}_2\text{H}$ ) and water, and the acids mentioned are formed by the simultaneous oxidation of this formic acid and further portions of the benzene, as expressed by the following equations :

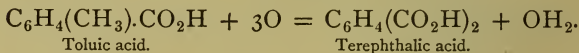
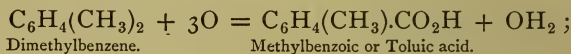


This is confirmed by the fact that increased quantities of benzoic and phthalic acids are obtained by oxidising a mixture of formic acid with benzene.

All the homologous hydrocarbons which are formed from benzene by a single operation, i.e., which are formed from it by the introduction of a single  $C_nH_{2n+1}$  group in the place of hydrogen, invariably yield the monobasic acid, *benzoic acid*, on oxidation ; thus :



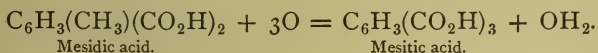
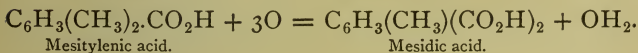
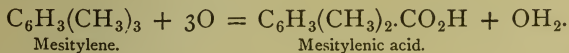
The oxidation of the hydrocarbons which may be regarded as di-derivatives of benzene, i.e., which are formed from it by the introduction of two  $C_nH_{2n+1}$  groups, may occur in two stages : in the first, a monobasic acid of the benzoic or  $C_6H_4(C_nH_{2n+1})CO_2H$  series is formed, one of the  $C_nH_{2n+1}$  groups remaining intact,<sup>1</sup> the other being oxidised to  $CO_2H$  ; in the second, the remaining  $C_nH_{2n+1}$  group is also similarly oxidised, and a dibasic acid<sup>2</sup> of the composition  $C_6H_4(CO_2H)_2$  produced. For example :



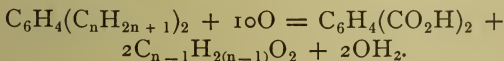
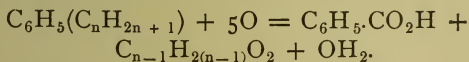
<sup>1</sup> On oxidation of the hydrocarbons derived from benzene by the introduction of two or more dissimilar  $C_nH_{2n+1}$  groups in place of hydrogen, it appears that the more complex—less stable—group is always the first to undergo oxidation ; thus  $C_6H_4(CH_3)C_3H_7$ , propylmethylbenzene, yields methylbenzoic (toluic) acid,  $C_6H_4(CH_3)CO_2H$ , and not propylbenzoic acid,  $C_6H_4(C_3H_7)CO_2H$ .

<sup>2</sup> One important exception to the latter part of this rule is to be noted. It appears that three isomeric modifications of each hydrocarbon of the form  $C_6H_4(C_nH_{2n+1})_2$  may exist, and that each of these yields the corresponding monobasic acid of the  $C_6H_4(C_nH_{2n+1})CO_2H$  series, but of the three isomeric acids thus formed, two only yield the corresponding dibasic acid on oxidation, the third is completely oxidised to water and carbonic anhydride by most oxidising agents (see xylene).

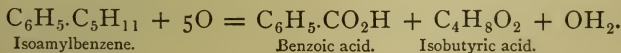
Similarly, the oxidation of the hydrocarbons which may be regarded as tri-derivatives of benzene, all of which appear to yield a tribasic acid of the composition  $C_6H_3(CO_2H)_3$ , as their final product, may occur in three stages. For example :



In short, the characteristic final oxidation product of a hydrocarbon of the benzene series of the general formula  $C_6H_{6-m}(C_nH_{2n+1})_m$ , however complex the  $C_nH_{2n+1}$  constituent, is always an acid of the form  $C_6H_{6-m}(CO_2H)_m$ . Hitherto too little attention has been paid to the products formed simultaneously with this acid, but it appears that in the case of the hydrocarbons formed by the aid of moniodoparaffins derived from primary monohydric alcohols,<sup>1</sup> an acid of the acetic series containing one unit of carbon less than the  $C_nH_{2n+1}$  constituent and water are produced, as represented by the following general equations :



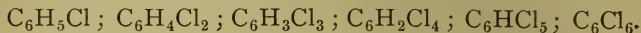
As a special instance, the oxidation of isoamylbenzene may be quoted ; thus :



<sup>1</sup> Moniodoparaffins other than those derived from primary monohydric alcohols have hitherto never been successfully employed in the preparation of hydrocarbons of the benzene series.



*Behaviour with Reagents.*—*Formation of Substitution Derivatives.*—Chlorine acts readily on benzene in presence of iodine or antimonie chloride, and gives rise to the following derivatives :



Bromine acts similarly, though less energetically. Iodo-derivatives are only obtained when the action of iodine takes place in presence of some substance capable of at once withdrawing the hydriodic acid, as it is formed, from the sphere of action ; such a substance is iodic acid. If the hydriodic acid be not withdrawn, it reacts on the iodo-derivative first formed and removes the iodine from it, replacing it by hydrogen :  $\text{C}_6\text{H}_6 + \text{I}_2 = \text{C}_6\text{H}_5\text{I} + \text{HI}$  ;  $\text{C}_6\text{H}_5\text{I} + \text{HI} = \text{C}_6\text{H}_6 + \text{I}_2$  ; but in presence of iodic acid it is at once reduced :  $\text{HIO}_3 + 5\text{HI} = 3\text{I}_2 + 3\text{OH}_2$ . Mono-, di-, and tri-iodobenzene have thus been prepared by heating benzene in closed tubes with iodine and iodic acid.

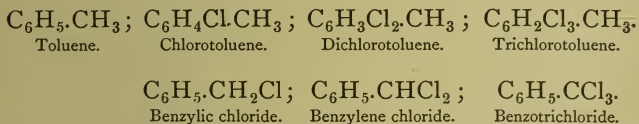
The haloid substitution-derivatives of benzene are characterised by their extreme stability and chemical indifference : thus nascent hydrogen (from sodium amalgam and water) is entirely without action on chloro- and bromobenzene, and these bodies even remain unaffected when fused with potassic hydrate. It is in this respect especially that these derivatives differ from the haloid derivatives of the paraffin and other intermediate series of hydrocarbons, all of which are acted upon by nascent hydrogen, alkalies, &c., with comparative readiness.

The homologues of benzene exhibit a remarkable behaviour with chlorine (and bromine). The first product of the action of chlorine on toluene *in the cold* is chlorotoluene,<sup>1</sup>  $\text{C}_7\text{H}_7\text{Cl}$ , a body which, like chlorobenzene, is in no way amenable to the action of ordinary reagents ; and by further similar treatment with chlorine, di- and trichlorotoluene, &c.,

<sup>1</sup> This chlorotoluene is a mixture of two isomeric bodies.

are formed, which are equally stable and indifferent compounds. If, however, chlorine be passed into *boiling* toluene, bodies of the same composition, but entirely different properties, are obtained : thus the first of these, benzylic chloride,  $C_7H_7Cl$ , is reconverted into toluene by the action of nascent hydrogen ; it readily exchanges Cl for (CN), (SCN), (SH), &c., when acted upon by KCN, KSCN, or KHS ; and is readily decomposed by alkalies. The second and third products of the composition  $C_7H_6Cl_2$  and  $C_7H_5Cl_3$ , obtained under the same conditions, exhibit analogous properties.

In explanation of this remarkable difference in the behaviour of the two series of products, the assumption is made that, in the case of the stable compounds, hydrogen in the so-called aromatic group is replaced by chlorine, whereas those formed by the action of chlorine at a high temperature contain the halogen in the  $C_nH_{2n+1}$  group, and the two series of derivatives of toluene are accordingly formulated as follows :



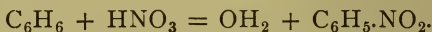
Moreover, an intermediate series of bodies can be obtained which it is generally assumed contain the chlorine partly in the aromatic and partly in the  $C_nH_{2n+1}$  group. Thus, if chlorotoluene be treated with chlorine at its boiling-point, or if benzylic chloride be acted upon by chlorine in the cold, a dichlorinated product is obtained, half the chlorine in which may be readily removed and replaced; the other half cannot. Hence this body is represented by the formula :  $C_6H_4Cl \cdot CH_2Cl$ . By the continued action of chlorine on this compound, at an elevated temperature, tri- and tetra-chlorinated derivatives are produced— $C_6H_4Cl \cdot CHCl_2$  and

$\text{C}_6\text{H}_4\text{Cl}.\text{CCl}_3$ , two-thirds and three-fourths of the chlorine in which respectively may be readily removed and replaced.

So far as our observations go, the higher homologues of benzene comport themselves similarly.

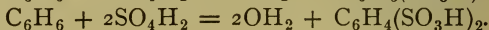
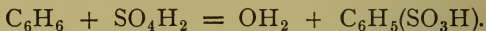
Most remarkable, however, is the fact that if the action of chlorine on toluene take place in presence of a small quantity of iodine, bodies of the first class *only* are obtained, no matter what the conditions of temperature.

Concentrated nitric acid converts benzene, with great evolution of heat, into nitrobenzene, which is converted by prolonged heating with the acid, or more readily if a mixture of concentrated nitric and sulphuric acids be employed, into a mixture of isomeric dinitrobenzenes,  $\text{C}_6\text{H}_4(\text{NO}_2)_2$  :

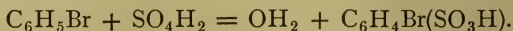


Similar nitro-derivatives are obtained from the homologous hydrocarbons. A weaker acid, however, exercises simply an oxidising action : thus diethylbenzene, for example, yields ethylbenzoic acid when boiled with diluted nitric acid.

By the action of concentrated sulphuric acid on benzene and its homologues, these hydrocarbons are converted into *sulphonic acids* ; e.g. :



The haloid substitution-derivatives of benzene and its homologues, excepting those formed from the latter by the action of chlorine or bromine on the boiling hydrocarbons, are similarly acted upon ; thus :



Bromobenzene.

Bromobenzenesulphonic acid.

When heated with a large excess of a concentrated hydriodic acid solution, for some hours, at  $270^\circ$ – $280^\circ$ , the aromatic hydrocarbons are converted into the corresponding paraffins (Berthelot). Baeyer finds, however, that dry hydriodic

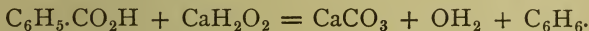
acid<sup>1</sup> has no action on benzene, even at 350°, but that it converts toluene into the hydrocarbon C<sub>7</sub>H<sub>10</sub>; xylene into C<sub>8</sub>H<sub>14</sub>; and mesitylene (trimethylbenzene) into C<sub>9</sub>H<sub>18</sub>.

BENZENE (*Benzol*; *Phenylic Hydride*<sup>2</sup>), C<sub>6</sub>H<sub>6</sub>.—*Formation*.

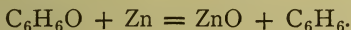
—1. By the action of heat on acetylene:  $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$ .

2. The higher homologues of benzene and a number of other hydrocarbons (naphthalene, anthracene, &c.), yield benzene among other products when strongly heated by passing through a red-hot tube, either alone or mixed with hydrogen.

3. Pure benzene is obtained by carefully distilling benzoic acid with calcic hydrate (slaked lime) at a dull red heat:



4. By passing phenol over strongly heated zinc dust:



On the large scale benzene is always prepared from the portion of coal-tar oil boiling below 100°. This is first shaken up with diluted sulphuric acid, then with water, and finally with soda solution, in order to remove all the substances of basic or acid properties it may contain. It is then fractionally distilled, and if required perfectly free from homologous<sup>3</sup> hydrocarbons and from hydrocarbons of the C<sub>n</sub>H<sub>2n+2</sub>, C<sub>n</sub>H<sub>2n</sub> and C<sub>n</sub>H<sub>2n-2</sub> series, with which it is always more or less contaminated and which cannot be separated by mere distillation, it is cooled to a low temperature by a refrigerating mixture of ice and salt; the benzene then crystallises out, whilst the other hydrocarbons remain liquid, and may for the greater part be removed by draining the crystals, which are afterwards melted and again caused to crystallise, and drained. The last traces of admixed hydrocarbons are removed by adding bromine until

<sup>1</sup> The hydrocarbon was enclosed in glass tubes with phosphonic iodide, PH<sub>4</sub>I, which is split up on heating into PH<sub>3</sub> + HI.

<sup>2</sup> The hypothetical radicle C<sub>6</sub>H<sub>5</sub>, derived from benzene, is termed *phenyl*.

<sup>3</sup> Commercial benzene always contains large quantities of toluene.

a permanent colouration is produced—the benzene being scarcely attacked by it, whereas the other hydrocarbons are acted upon and converted into brominated derivatives—then washing with alkali, drying over solid potassic hydrate, and rectifying, when pure benzene boiling constantly at  $81^{\circ}$  is obtained.

Benzene is a colourless, limpid, strongly refracting, highly inflammable liquid of peculiar odour ; specific gravity  $\cdot 899$  at  $0^{\circ}$ . It solidifies, on cooling, to a brilliant white mass of fern-like tufts, which melt at  $5^{\circ}\cdot 5$  ; it is scarcely soluble in water, but is a solvent of a very large number of bodies.

*Derivatives of Benzene.*—Chlorine is without action on benzene in the dark, or in diffused light ; the action of chlorine or bromine in bright sunlight, however, gives rise to the formation of additive compounds of the formula  $C_6H_6Cl_6$  (benzene hexachloride) and  $C_6H_6Br_6$  (benzene hexabromide). These are white crystalline substances, which are converted into trichloro- and tribromobenzene respectively, by the action of potassic hydrate, thus :



By passing chlorine into benzene in which some iodine is dissolved and heating gently meanwhile, the following series of derivatives are obtained :<sup>1</sup>

|                            | Formula.     | Boiling Point. | Melting Point. |
|----------------------------|--------------|----------------|----------------|
| Monochlorobenzene          | $C_6H_5Cl$   | $133^{\circ}$  | $-40^{\circ}$  |
| Paradichlorobenzene        | $C_6H_4Cl_2$ | $172^{\circ}$  | $53^{\circ}$   |
| Orthodichlorobenzene       | $C_6H_4Cl_2$ | $179^{\circ}$  | liq.           |
| 1 : 2 : 4 Trichlorobenzene | $C_6H_3Cl_3$ | $213^{\circ}$  | $16^{\circ}$   |

<sup>1</sup> The action of iodine in assisting the formation of chlorobenzenes is explained by the fact that iodine chloride readily acts on benzene: apparently, moniodobenzene is first produced:  $C_6H_6 + ICl = C_6H_5I + HCl$ , but this is converted by the action of a further portion of the chloride into chlorobenzene:  $C_6H_5I + ICl = C_6H_5Cl + I_2$ . The iodine thus set free is again converted into chloride by the chlorine, and thus acts as a carrier of the chlorine.

|                                           | Formula.     | Boiling Point. | Melting Point. |
|-------------------------------------------|--------------|----------------|----------------|
| 1 : 2 : 4 : 5 Tetrachloro-benzene . . . . | $C_6H_2Cl_4$ | 240°           | 139°           |
| Pentachlorobenzene . . . .                | $C_6HCl_5$   | 276°           | 85°            |
| Hexachlorobenzene . . . .                 | $C_6Cl_6$    | 326°           | 226°           |

The following have been prepared by indirect methods :

|                                           | Formula.     | Boiling Point. | Melting Point. |
|-------------------------------------------|--------------|----------------|----------------|
| Metadichlorobenzene . . . .               | $C_6H_4Cl_2$ | 172°           | liq.           |
| 1 : 2 : 3 Trichlorobenzene . . . .        | $C_6H_3Cl_3$ | 218°           | 54°            |
| 1 : 3 : 5 Trichlorobenzene . . . .        | $C_6H_3Cl_3$ | 209°           | 63°            |
| 1 : 2 : 3 : 4 Tetrachloro-benzene . . . . | $C_6H_2Cl_4$ | 254°           | 45°            |
| 1 : 3 : 4 : 5 Tetachloro-benzene . . . .  | $C_6H_2Cl_4$ | 246°           | 50°            |

The indirect methods by which these are produced are three in number, viz. :

1. By the action of  $PCl_5$  on the chloro-derivatives of phenol (p. 167), thus :  $C_6H_2Cl_3.OH + PCl_5 = C_6H_2Cl_4 + POCl_3 + HCl$ .

2. By submitting the chlorinated derivatives of amidobenzene or aniline (p. 333) to the action of nitrous acid and treating the resulting diazo-compounds with alcohol (see p. 334); or by simply acting on these same chlorinated anilines with ethylic nitrite, e.g. :  $C_6H_2Cl_3.NH_2 + C_2H_5NO_2 = C_6H_3Cl_3 + N_2 + C_2H_4O + OH_2$ .

3. By converting the chlorinated derivatives of amidobenzene into diazo-chlorides, and distilling the platinum double salts of these chlorides :  $(C_6H_3Cl_2.N_2)_2PtCl_6 = 2C_6H_3Cl_3 + 2N_2 + Pt + 2Cl_2$ .

By the direct action of bromine on benzene, bromobenzenes are produced corresponding to the chlorobenzenes obtained by the action of chlorine, and others may be formed by indirect methods similar to those employed in the preparation of the corresponding chlorobenzenes.

Crude dinitrobenzene (p. 120) is a mixture of three iso-



merides all of which crystallise well, viz. : *Paradinitrobenzene*, which melts at  $171^{\circ}$ ; *Metadinitrobenzene*, which melts at  $89^{\circ}$ ; and *Orthodinitrobenzene*, which melts at  $118^{\circ}$ . By treating metadinitrobenzene with a mixture of the strongest nitric acid and pyrosulphuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ) in sealed tubes at  $140^{\circ}$ , *trinitrobenzene*,  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ , is said to be produced.

A large number of *nitro-haloid* derivatives are formed by treating the various haloid derivatives of benzene with nitric acid.

Nitrobenzene is converted into *amidobenzene*, *phenylamine* or *aniline*,  $\text{C}_6\text{H}_5\text{NH}_2$ , by the action of reducing agents (sources of nascent hydrogen), the group  $\text{NO}_2$  being converted into the  $\text{NH}_2$  or amidogen group (see p. 330). In a similar manner, the dinitrobenzenes are converted into corresponding *diamidobenzenes* or *phenylenediamines*; and the nitro-haloid derivatives into corresponding *amido-haloid* derivatives.<sup>1</sup>

It is especially noteworthy that in no case have isomeric modifications of mono-derivatives of benzene been obtained; thus, we only know one methylbenzene (toluene), one chlorobenzene, one bromobenzene, one nitrobenzene. The greatest number of isomeric modifications of di-derivatives of benzene which have been obtained is three; whilst of many of the tri-derivatives no less than six isomeric forms have been prepared.

TOLUENE (*Methylbenzene*),  $\text{C}_7\text{H}_8 = \text{C}_6\text{H}_5\text{CH}_3$ , may be produced by treating a mixture of monobromobenzene and iodomethane with sodium, but it is usually obtained by the fractional distillation of that portion of coal-tar oil which boils at  $100^{\circ}$ – $120^{\circ}$ . It is a mobile colourless liquid, boiling at  $111^{\circ}$ . Toluene yields benzoic acid,  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ , and water on oxidation.

In nearly every instance, two isomeric derivatives are formed simultaneously by the action of various reagents on

<sup>1</sup> For a full account of the benzene derivatives the student should consult Watts' *Dictionary of Chemistry*, vols. i. vi. vii. and viii.

toluene. Thus two monobromotoluenes are produced by the action of bromine *in the cold*: one of these is a crystalline solid, and yields *parabromobenzoic acid*,  $C_6H_4Br.CO_2H$ , on oxidation; the other is liquid and is entirely decomposed on oxidation. Similarly, two isomeric monochlorotoluenes are formed by the action of chlorine in the cold, and treatment of toluene with nitric acid gives rise to two mononitrotoluenes: the one being crystalline and convertible into *paranitrobenzoic acid*,  $C_6H_4(NO_2).CO_2H$ ; the other liquid and entirely decomposed by oxidising agents. Again, two isomeric toluenesulphonic acids, readily distinguishable by the different crystalline forms, &c., of their potassic salts, are formed on dissolving toluene in concentrated sulphuric acid.

XYLENE,  $C_8H_{10}$ .—*Ethylbenzene*,  $C_6H_5.C_2H_5$ , prepared by the action of sodium on a mixture of monobromobenzene with iodethane, boils at  $135^\circ$ ; it yields benzoic acid, carbonic anhydride and water on oxidation.

Three isomeric modifications of the metameric compound dimethylbenzene,  $C_6H_4(CH_3)_2$ , have been obtained, namely, *Para*-, *Meta*- and *Ortho*-xylene. These are all present in coal-tar oil.

*Paraxylene* is prepared synthetically by the action of sodium on a mixture of iodomethane with the crystalline modification of monobromotoluene; it forms white crystals, which melt at  $15^\circ$  and boil at  $136^\circ$ ; it is converted into *paratoluic acid*,  $C_6H_4(CH_3).CO_2H$ , on oxidation, which, on further oxidation, yields *terephthalic acid*,  $C_6H_4(CO_2H)_2$ .

*Metaxylene*, which appears to be the chief constituent of coal-tar oil xylene, is obtained by distilling mesitylenic acid with lime:  $C_6H_3(CH_3)_2.CO_2H + CaO = C_6H_4(CH_3)_2 + CaCO_3$ . Metaxylene boils at  $137^\circ$ – $138^\circ$ ; it yields *metatoluic acid* on oxidation, which in turn yields *isophthalic acid*.

*Orthoxylene*.—By the action of sodium on a mixture of iodomethane with the monobrominated derivative of either para- or metaxylene, the same modification of trimethylbenzene is obtained. By digestion with dilute nitric acid

this *pseudocumene*, as it is termed, is converted into a mixture of two isomeric acids, known as *xylic* and *paraxylic* acids. Xylic acid,  $\text{C}_6\text{H}_3(\text{CH}_3)_2\cdot\text{CO}_2\text{H}$ , furnishes metaxylene on distillation with lime, whilst paraxylic acid yields orthoxylene when similarly treated. Orthoxylene boils at  $140^\circ\text{--}141^\circ$ ; on oxidation by dilute nitric acid it yields *orthotoluic* acid, which it was long supposed could not be oxidised to the corresponding dibasic acid, *phthalic acid*, but it appears that this can be done if the proper oxidising agent—an alkaline solution of potassic permanganate—is employed. The three isomeric oxylenes also differ in their behaviour with bromine, concentrated nitric acid, and sulphuric acid, furnishing isomeric substitution derivatives differing considerably in properties.

MESITYLENE and PSEUDOCUMENE.—Coal-tar oil contains two isomeric *trimethylbenzenes*, known as mesitylene and pseudocumene. A remarkable synthetic method of preparing the former consists in distilling dimethylketone or acetone,  $\text{CO}(\text{CH}_3)_2$ , with sulphuric acid. In this reaction the acetone appears to be converted by the withdrawal of the elements of water into methylacetylene (allylene),  $\text{HC}:\text{C}(\text{CH}_3)$ , which combines with the acid. The acid sulphate thus produced is no sooner formed than it decomposes, but the allylene which it probably yields does not escape as such, but at the moment of liberation forms mesitylene:  $3\text{C}_2\text{H}(\text{CH}_3)=\text{C}_6\text{H}_3(\text{CH}_3)_3$ . The two hydrocarbons are distinguished by their conversion into isomeric acids on oxidation, and especially also by their behaviour with concentrated nitric acid, mesitylene yielding a *trinitro*-derivative,  $\text{C}_6(\text{NO}_2)_3(\text{CH}_3)_3$ , which melts at  $232^\circ$ , and pseudocumene an isomeride melting at  $185^\circ$ .

TETRA-, PENTA- and HEXA-METHYLBENZENES.—If methylic chloride,  $\text{CH}_3\text{Cl}$ , is passed into a warm solution of aluminic chloride,  $\text{Al}_2\text{Cl}_6$ , in benzene, hydrochloric acid gas is evolved, and methylbenzene or toluene is produced:  $\text{CH}_3\text{Cl} + \text{C}_6\text{H}_6 = \text{C}_6\text{H}_5\cdot\text{CH}_3 + \text{HCl}$ . Methylic chloride

alone is entirely without action on benzene ; the nature of the influence which aluminic chloride exercises is not yet understood, however. By continuing the action, higher methylated benzenes and finally hexamethylbenzene are formed. The dimethylbenzene produced in this manner consists of metaxylene mixed with a very small amount of paraxylene ; both mesitylene and pseudocumene are formed, but the latter is the chief product ; two tetramethylbenzenes are also formed, one crystalline, the other liquid ; a single penta- and a single hexa-methylbenzene are obtained. Penta-methylbenzene boils at about  $230^{\circ}$ , and is a crystalline solid at low temperatures ; hexamethylbenzene,  $C_6(CH_3)_6$ , melts at about  $150^{\circ}$  and boils at about  $260^{\circ}$  ; unlike all other hydrocarbons of the series, the latter does not form a sulpho-acid when treated with sulphuric acid.

CUMENE and CYMENE.—Cumin oil, distilled from the seeds of *Cuminum cyminum*, consists chiefly of cymene and cumic aldehyde,  $C_{10}H_{12}O$  (p. 235). The formation of *cymene* from the terpenes, citrenes, and camphor has already been described ; it may be prepared synthetically by the action of sodium on a mixture of parabromotoluene,  $C_6H_4Br.CH_3$ , and normal propylic bromide,  $CH_3.CH_2.CH_2Br$  ; on oxidation, it yields first paratoluic and then terephthalic acid.

By oxidising cumic aldehyde, and distilling the resulting cumic acid,  $C_3H_7^{\beta}.C_6H_4.COOH$ , with baric hydrate, *cumene* or isopropylbenzene is produced ; this hydrocarbon yields benzoic acid on oxidation. By acting on a mixture of bromocumene and methylic iodide with sodium, *methylisopropylbenzene* isomeric with methylpropylbenzene or cymene is obtained. The two hydrocarbons are readily distinguished by means of their sulpho-acids.

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The behaviour of benzene and its homologues shows that the hydrocarbons of this series are of an altogether different type from those of the series previously considered. The

following is the symbol devised by Kekulé to express the peculiar behaviour of benzene :



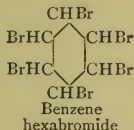
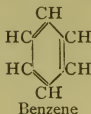
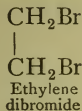
It will be noticed that the carbon symbols are represented as united in the form of a 'closed chain' or ring, whereas in the formulæ of the paraffins and hydrocarbons of the ethylene and acetylene series the carbon symbols are always represented as united in the form of an 'open chain.'

This symbol is chiefly based on the observation (1) that benzene unites with at most six unit-weights of chlorine or bromine ; and (2) that it is incapable of forming isomeric *mono*-substitution derivatives.

1. On combining the hydrocarbons of the  $C_nH_{2n}$  and  $C_nH_{2n-2}$  series, or valylene,  $C_5H_6$ , with the maximum amount of chlorine or bromine, the amount of halogen taken up by the hydrocarbon is always equivalent to the amount of hydrogen which would be withdrawn in its formation from the corresponding paraffin ; the resulting haloid compound, in fact, is always a paraffin derivative. Thus, ethylene and bromine form a dibromethane ; acetylene and bromine a tetrabromethane ; and valylene and bromine a hexabromopentane. But benzene forms only a hexachloride and hexabromide ; whereas, if similar in constitution to the 'open chain' hydrocarbons, since it contains eight unit weights of hydrogen less than the corresponding paraffin,  $C_6H_{14}$ , it should form an octobromide. By assuming, however, that the carbon symbols are associated in the manner shown in the above symbol, this behaviour of benzene no longer appears peculiar. The addition of bromine takes place in precisely the same manner as in the formation of ethylene dibromide from ethylene, but as there are three pairs of carbon symbols in the benzene formula similar to the single pair in the formula of ethylene, three times as much bromine

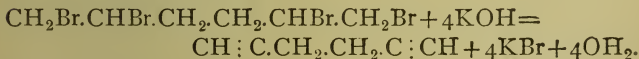


is taken up by benzene as by ethylene ; a comparison of the following formulæ will render this more evident :



The separation of carbon from carbon when it is associated in the manner represented by the formula of ethylene dibromide is never effected by means of chlorine or bromine, except these agents are employed in excess and at a relatively very high temperature ; it will be obvious from the formula of benzene hexabromide that the formation of an octobromide from benzene could not be realised without such a separation taking place.

This hypothesis is further supported by the fact that a hydrocarbon, known as *dipropargyl*, exists, isomeric with benzene, possessing the properties of an 'open chain' hydrocarbon, and capable of forming an octobromide. Dipropargyl is formed by the action of potassic hydrate on diallyltetrabromide (p. 104), thus :

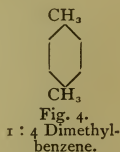
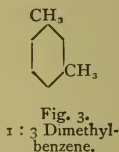
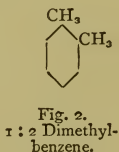


It is a mobile liquid boiling at about  $85^\circ$ , which produces a white precipitate,  $\text{C}_6\text{H}_4(\text{Ag}_2) + 2\text{OH}_2$ , in an ammoniacal solution of argentic nitrate and a greenish-yellow precipitate,  $\text{C}_6\text{H}_4(\text{Cu}_2) + 2\text{OH}_2$ , in an ammoniacal solution of a cuprous salt. Bromine combines with it with explosive violence forming an oily tetrabromide, which on further treatment with bromine yields a crystalline octobromide.

2. It will be observed that the formula given to benzene is perfectly symmetrical, and hence the same formula will always result whichever of the hydrogen symbols is displaced by any one particular monad radicle ; in other words, no isomeric mono-derivatives of benzene are possible, and in



point of fact none have been obtained. This is no longer the case, however, if two identical or different monad radicles are substituted for two of the hydrogen symbols ; several formulæ may then be constructed in which the two radicles occupy relatively different positions. Thus, indicating the several hydrogen symbols as  $H^1$ ,  $H^2$ ,  $H^3$ ,  $H^4$ ,  $H^5$ , and  $H^6$ , if the radicle  $X'$  be introduced in place of  $H^1$ , then isomerides will be formed by introducing the same radicle, or a different radicle  $Y'$ , in place of either  $H^2$ , or  $H^3$ , or  $H^4$  ; but these are the only possible isomerides since  $H^2$  and  $H^6$ , and  $H^3$  and  $H^5$ , respectively are identically situated relatively to  $H^1$ . The three isomerides may be spoken of as the 1 : 2, 1 : 3, and 1 : 4 derivatives ; in writing their formulæ, it is convenient to employ a simple hexagon in place of the symbol for benzene previously used, merely the formulæ of the radicles introduced being written in the appropriate positions at the angles of the figure, and the positions always numbered in the order indicated in fig. 1. If  $X' = CH_3$ , we have the formulæ of the three dimethylbenzenes, as shown in figs. 2, 3, and 4 :



The 1 : 2 di-derivatives are commonly spoken of as *ortho*-, the 1 : 3 as *meta*-, and the 1 : 4 as *para*- compounds, the three dimethylbenzenes represented by figs. 2, 3, and 4 being respectively identical with *ortho*-, *meta*-, and *para*-xylene.

In a similar manner, it may be shown that three isomeric tri- and three isomeric tetra-derivatives may be formed by the introduction of  $X'$  ; but isomeric penta- or hexa-derivatives of this kind are not possible. A greater number of isomeric tri- and tetra-, and also isomeric penta- and hexa-

derivatives may be produced, however, by the introduction of dissimilar radicles.

It will be seen on comparing the following symbols of all the possible di- and tri-bromobenzenes, that the three tri-bromobenzenes cannot all be derived from each of the dibromobenzenes; and that while the 1 : 3 modification may give rise to the formation of all *three* tribromobenzenes, only *two* of these latter can be obtained from the 1 : 2 modification and only *one* from the 1 : 4 modification :

Dibromobenzenes.



1 : 2



1 : 3



1 : 4

Tribromobenzenes.



1 : 2 : 4



1 : 2 : 3



1 : 2 : 3



1 : 3 : 5



1 : 3 : 4  
or 1 : 2 : 4



1 : 2 : 4

Hence, by ascertaining which of the tribromobenzenes can only be procured from one of the dibromobenzenes, it is possible to ascertain which of these latter is the 1 : 3 modification. If it be then established which two dibromobenzenes alone can furnish a second tribromobenzene, it is possible to differentiate the 1 : 2 and 1 : 3 modifications of the former from the 1 : 4 modification, and as it is known which is the 1 : 3 modification, we are able to say which is the 1 : 2 modification. As only three are possible, the remaining modification must be the 1 : 4 dibromobenzene. On the other hand, it follows that the tribromobenzene which can only be obtained from one dibromobenzene is the 1 : 3 : 5 variety; that which can be produced from two is the 1 : 2 : 3 modification; and the remaining isomeride is therefore the 1 : 2 : 4 derivative. The train of reasoning here indicated has been experimentally realised by Körner.

His conclusions have been verified in many ways by other chemists ; and at present, notwithstanding the vast amount of labour which during the past few years has been expended on the investigation of the benzene derivatives, there is not a single fact known which does not harmonise with Kekulé's hypothesis of the 'constitution' of benzene and its derivatives.

The position of the radicles in the formulæ of the three dibromobenzenes being known, it is easy to ascertain the formulæ of other di-derivatives either by preparing them from the dibromobenzenes, or *vice versâ*, by preparing the dibromobenzenes from them. Thus 1 : 4 or *para-dibromobenzene* is converted into *paraxylene*,  $C_6H_4(CH_3)_2$ , on treatment with sodium and methylic iodide, and paraxylene yields *paratoluic* and *terephthalic acids* on oxidation ; paraxylene, paratoluic, and terephthalic acids are therefore 1 : 4 derivatives of benzene. By the action of sodium on a mixture of ethylic chlorocarbonate,  $Cl.COOC_2H_5$ , and 1 : 3 or *metadibromobenzene*, the ethylic salt of *isophthalic acid* is obtained ; but *metatoluic* and isophthalic acids are oxidation products of *metaxylene* : hence metaxylene, metatoluic and isophthalic acids are 1 : 3 derivatives of benzene. Consequently orthoxylene, orthotoluic acid and phthalic acid are 1 : 2 derivatives of benzene.

The formulæ of all other di-derivatives, and also of the higher derivatives, of benzene, may be established by similar reasoning.

#### $C_nH_{2n-8}$ SERIES OF HYDROCARBONS.

Three hydrocarbons of this series are known:—

|                               |                     |
|-------------------------------|---------------------|
| Cinnamene or phenylethylene . | $C_6H_5.CH=CH_2$    |
| Allylbenzene . . . . .        | $C_6H_5.CH=CH.CH_3$ |
| Phenylbutylene . . . . .      | $C_6H_5.C_4H_7$     |

CINNAMENE,  $C_8H_8$ , may be produced (1) by strongly heating acetylene :  $4C_2H_2=C_8H_8$  ; (2) by the action of

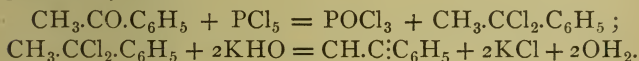
potassic hydrate on bromethylbenzene,  $C_6H_5 \cdot CHBr \cdot CH_3$ ; and (3) by distilling cinnamic acid,  $C_6H_5 \cdot C_2H_2 \cdot COOA$ , with baric hydrate. It is present ready formed in liquid storax, and may be separated by distilling the balsam with water. Cinnamene is a colourless, mobile, strongly refracting liquid, boiling at  $145^\circ$ . It combines directly with chlorine and bromine to form the additive compounds cinnamene dichloride,  $C_8H_8Cl_2$ , and cinnamene dibromide,  $C_8H_8Br_2$ , the analogues of ethylene-dichloride and dibromide. If heated to  $200^\circ$  in a closed tube, it is converted into the polymeric *metacinnamene*.

#### $C_nH_{2n-10}$ SERIES OF HYDROCARBONS.

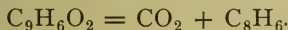
ACETENYLBENZENE,  $C_8H_6$ , the only known hydrocarbon of the series, is obtained—1. By the action of an alcoholic solution of potassic hydrate on cinnamene dibromide :



2. By distilling methylphenylketone with phosphorus pentachloride and treatment of the resulting compound with potassic hydrate :



3. By heating phenylpropionic acid with water at  $120^\circ$  :

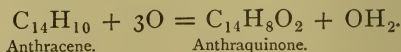


Acetenylbenzene is a colourless, strongly refracting liquid, of peculiar aromatic odour; it boils at  $139^\circ$ . It has the property so characteristic of acetylene and some of its homologues, of precipitating metallic solutions : thus it produces a yellow precipitate of the composition  $(C_8H_5)_2Cu_2$ , in an ammoniacal solution of cuprous chloride; and the compound  $C_8H_5Na$  is produced with evolution of hydrogen on the addition of sodium to an ethereal solution of acetenylbenzene. This sodium derivative unites readily with car-

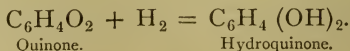
bonic anhydride to form the sodic salt of phenylpropionic acid:  $C_8H_5Na + CO_2 = C_9H_5NaO_2$ . On agitating the copper derivative suspended in ammonia with oxygen, the following reaction occurs:  $(C_8H_5)_2Cu_2 + O = C_{16}H_{10} + Cu_2O$ . The new hydrocarbon, *diacetylnylbenzene*, crystallises in long white needles, which melt at  $97^\circ$ .

$C_nH_{2n-12}$ ,  $C_nH_{2n-18}$  AND  $C_nH_{2n-24}$  SERIES OF  
HYDROCARBONS.

*Naphthalene*,  $C_{10}H_8$ ; *Anthracene*,  $C_{14}H_{10}$ ; and *Chrysene*,  $C_{18}H_{12}$ , which are respectively the representatives of the above three series, may be regarded as the successive terms of a homologous series, of which *benzene*,  $C_6H_6$ , is the first member, and in which there is a difference of  $C_4H_2$  between the homologues. In fact, great analogy in chemical behaviour exists between these four bodies, and they also differ greatly in chemical behaviour from most other series. Especially characteristic of these hydrocarbons is the property of forming so-called *quinones*. These quinones are invariably products of oxidation, but whereas in all ordinary cases of oxidation the reaction consists in the replacement of  $H_2$  by  $O$ , as in the formation of acetic acid from alcohol, for example:  $C_2H_6O + 2O = C_2H_4O_2 + OH_2$ , in the formation of the quinones no less than two units of oxygen are introduced into the compound for every two units of hydrogen removed, e.g.:



These quinones are neutral bodies; they are readily converted by the action of nascent hydrogen into the corresponding *hydroquinones*, which are the dioxy-derivatives of the hydrocarbons from which the quinones are produced, e.g.:



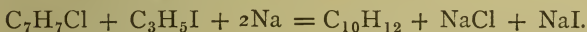
Benzene cannot be directly oxidised to the corresponding

quinone, but chlorinated quinones may readily be obtained directly : thus chlorochromic anhydride,  $\text{CrO}_2\text{Cl}_2$ , a reagent which exercises simultaneously an oxidising and a chlorinating action, converts benzene into *trichloroquinone* :



NAPHTHALENE,  $\text{C}_{10}\text{H}_8$ , the primary member of the  $\text{C}_n\text{H}_{2n-12}$  series, is one of the principal by-products in the manufacture of coal gas. It is a constant product of the decomposition of many hydrocarbons by a red heat, and it is also formed when a mixture of benzene, cinnamene, or anthracene vapour with ethylene gas is passed through a red-hot tube ; in fact, it is generally produced when organic bodies are distilled out of contact with air at very high temperatures.

The synthesis of naphthalene has recently been effected in the following manner : a mixture of benzylic chloride with allylic iodide when acted upon by sodium yields the hydrocarbon  $\text{C}_{10}\text{H}_{12}$  (*phenylbutylene*), thus :



This hydrocarbon combines directly with bromine, and the resulting dibromide is resolved into naphthalene, hydrogen, and hydrobromic acid on passing its vapour over quicklime heated to redness :  $\text{C}_{10}\text{H}_{12}\text{Br}_2 = \text{C}_{10}\text{H}_8 + \text{H}_2 + 2\text{HBr}$ .

Naphthalene crystallises in brilliant white scales ; it melts at  $79^\circ$  and boils at  $216^\circ$ . It possesses a peculiar unpleasant odour, is insoluble in water, but dissolves readily in alcohol, ether, fatty and essential oils, and in acetic acid.

Naphthalene closely resembles benzene in chemical behaviour. Bromine converts it, according to the proportions used, and to the temperature to which the mixture is heated, into one or other of the following compounds :



By the action of chlorine both substitution-derivatives and additive compounds are obtained, namely :



|                           |   |                                          |                 |
|---------------------------|---|------------------------------------------|-----------------|
| Substitution-derivatives. | { | Monochloronaphthalene . . .              | $C_{10}H_7Cl$   |
|                           |   | Dichloronaphthalene . . .                | $C_{10}H_6Cl_2$ |
|                           |   | Trichloronaphthalene . . .               | $C_{10}H_5Cl_3$ |
|                           |   | Tetrachloronaphthalene . . .             | $C_{10}H_4Cl_4$ |
|                           |   | Pentachloronaphthalene . . .             | $C_{10}H_3Cl_5$ |
| Additive compounds        | { | Naphthalenetetrachloride . . .           | $C_{10}H_8Cl_4$ |
|                           |   | Monochloronaphthalenetetrachloride . . . | $C_{10}H_7Cl_5$ |
|                           |   | Dichloronaphthalenetetrachloride . . .   | $C_{10}H_6Cl_6$ |

By the action of chlorine in presence of antimonious chloride it is finally converted into octochloronaphthalene,  $C_{10}Cl_8$ .

Nitric acid converts naphthalene into nitronaphthalene,  $C_{10}H_7.NO_2$ , and by continued treatment into di-, tri-, and finally tetranitronaphthalene; of these latter several isomeric modifications are produced simultaneously.

Treated with chromic anhydride in acetic acid solution, it is oxidised to naphthoquinone :



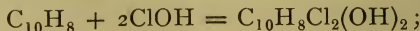
On oxidation with potassic dichromate and sulphuric acid, it yields *dinaphthyl* :  $2C_{10}H_8 + O = C_{20}H_{14} + OH_2$ ; and at the same time phthalic acid is formed :  $C_{10}H_8 + 9O = C_8H_6O_4 + 2CO_2 + OH_2$ .

An isomeride of dinaphthyl, of higher melting-point, is obtained on passing naphthalene vapour through a tube heated to bright redness :  $2C_{10}H_8 = C_{20}H_{14} + H_2$ ; dinaphthyl melts at  $154^\circ$ , isodinaphthyl at  $187^\circ$ .

Naphthalene dissolves readily in warm concentrated sulphuric acid with formation of two isomeric ( $\alpha$  and  $\beta$ ) *naphthalenesulphonic acids* :



Naphthalene combines directly with hypochlorous acid:



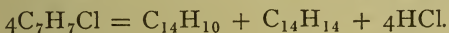
the product being acted upon by alkalis thus :



Only two homologues of naphthalene are known: *methylnaphthalene*,  $C_{11}H_{10} = C_{10}H_7 \cdot CH_3$ , and *ethylnaphthalene*,  $C_{12}H_{12} = C_{10}H_7 \cdot C_2H_5$ , obtained respectively by the action of sodium on mixtures of bromonaphthalene with iodomethane, or iodethane. The former boils at  $231^\circ$ , the latter at  $251^\circ$ ; both are liquid even at  $-14^\circ$ ; they are entirely decomposed on oxidation, and do not seem capable of furnishing any well-characterised derivatives.

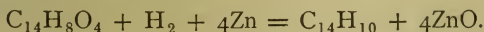
ANTHRACENE,  $C_{14}H_{10}$ , the primary member of the  $C_nH_{2n-18}$  series of hydrocarbons, has lately attained to great importance, owing to its forming the starting-point for the artificial production of *alizarin*, the colouring matter contained in madder root (*Rubia tinctorum*), one of the most valuable dyeing materials with which we are acquainted.

Anthracene is obtained on the large scale from the portion of the solid product of the distillation of coal-tar which passes over at about  $340^\circ$ – $400^\circ$ . It may be produced artificially—1. By heating benzylic chloride with water to  $200^\circ$ , together with the hydrocarbon benzyltoluene,  $C_{14}H_{14}$ :



2. By the action of heat on various hydrocarbons, or mixtures of hydrocarbons: thus benzyltoluene is resolved into anthracene and hydrogen when passed through a red-hot tube; and some anthracene is obtained when toluene vapour is similarly treated, its production being doubtless preceded by that of benzyltoluene. A mixture of benzene vapour with ethylene also yields anthracene when passed through a red-hot tube.

3. By heating alizarin with zinc-dust, the necessary hydrogen being probably furnished by the entire decomposition of a portion of the alizarin:



4. A number of other vegetable products, such as *chrysophanic acid*— $C_{14}H_8O_4$ , *aloin*, *frangulic acid*— $C_{14}H_{10}O_5$ , &c., also yield anthracene on distillation with zinc-dust.

Anthracene forms dazzling white four- or six-sided tables, which exhibit a magnificent violet fluorescence ; it melts at  $213^{\circ}$  and boils at about  $360^{\circ}$ . By prolonged exposure to sunlight it undergoes a remarkable physical alteration, being converted into so-called *paranthracene*, which melts at  $244^{\circ}$  and differs in many respects from ordinary anthracene, but is reconverted into anthracene on fusion.

Anthracene combines with nascent hydrogen (from sodium amalgam and alcohol), forming anthracene dihydride, and if heated with hydriodic acid and phosphorus to  $200^{\circ}$ – $220^{\circ}$ , it is converted into anthracene hexhydride,  $C_{14}H_{16}$ . At a red heat the latter is resolved into anthracene and hydrogen.

The products of the action of bromine on anthracene are di-, tri-, and tetrabromanthracene, and dibromanthracene-tetrabromide,  $C_{14}H_8Br_6$ .

Anthracene is readily oxidised to anthraquinone by the action of nitric acid, or of a mixture of potassic dichromate with sulphuric acid :  $C_{14}H_{10} + 3O = C_{14}H_8O_2 + OH_2$ .

Anthraquinone is also obtained by oxidising dichlor- or dibromanthracene :  $C_{14}H_8Cl_2 + O_2 = C_{14}H_8O_2 + Cl_2$ .

Anthraquinone is readily converted by the action of bromine into dibromanthraquinone ; if this body be carefully fused with potassic hydrate, the mass assumes a violet colour, and then contains the potassium derivative of alizarin (dioxanthraquinone) ; thus :



On the addition of an acid to the aqueous solution of the fused mass, the crude alizarin is thrown down as a yellow precipitate, and may be obtained pure by carefully subliming the dry precipitate, in the form of beautiful red prisms. Alizarin dissolves readily in alkalies or alkaline carbonates forming deep purple-coloured solutions.

In manufacturing alizarin on the large scale, sulphuric acid is employed instead of bromine ; but when it is prepared in this manner several other bodies are also formed, viz.

two dioxyanthraquinones isomeric with alizarin, called *anthraflavic* and *isoanthraflavic acid*; and two trioxyanthraquinones,  $C_{14}H_5O_2(OH)_3$ , *anthrapurpurin* and *flavopurpurin*, isomeric with the purpurin which accompanies alizarin in the madder root. The formation of these different bodies is accounted for in the following manner. The first product of the action of sulphuric acid on anthraquinone is *anthraquinone-monosulphonic acid*,  $C_{14}H_7O_2(SO_3H)$ ; on heating the sodic salt of this acid with sodic hydrate, the group  $SO_3Na$  is replaced by the group  $ONa$ , and the sodic derivative of *monoxyanthraquinone*,  $C_{14}H_7O_2(OH)$ , is produced, but on further heating, this latter undergoes conversion into sodic alizarate:  $C_{14}H_7O_2(ONa) + NaOH = C_{14}H_6O_2(ONa)_2 + H$ . By the continued action of the acid on anthraquinone, a mixture of two isomeric disulpho-acids is produced which are distinguished by yielding sodic salts of different solubility. By fusing the less soluble sodic salt with sodic hydrate, sodic anthraflavate is produced; and the more soluble salt, when similarly treated, yields sodic isoanthraflavate. Like sodic alizarate, however, these products are both further acted upon by the sodic hydrate, the former being converted into flavopurpurate and the latter into anthrapurpurate.

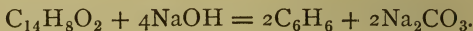
By heating anthracene with nitric acid, anthraquinone is first formed, but is converted, on further heating, into dinitroanthraquinone. This body has the property of combining with all the solid hydrocarbons present in coal-tar, forming crystalline compounds which are readily decomposed by alkalies; thus it unites with anthracene to form the compound  $C_{14}H_{10}.C_{14}H_6(NO_2)_2O_2$ .

Coal-tar oil also contains an isomeride of anthracene termed *phenanthrene*, which closely resembles anthracene in appearance, but melts at  $100^\circ$  and boils at  $340^\circ$ , and is further characterised and distinguished from anthracene by its behaviour on oxidation, whereby it is first converted into a quinone,  $C_{14}H_8O_2$ , isomeric with anthraquinone, which,

on further oxidation, yields a dibasic acid of the formula  $C_{14}H_8O_4$  (*diphenic acid*). Anthraquinone cannot be further oxidised. On distillation over soda-lime heated to redness, phenanthraquinone yields diphenyl,  $C_{12}H_{10}$ , thus :

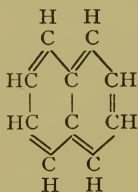


whilst anthraquinone, when similarly treated, yields benzene:

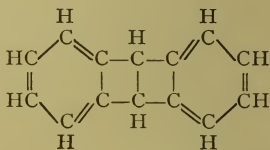


Phenanthrene forms with bromine a crystalline dibromide.

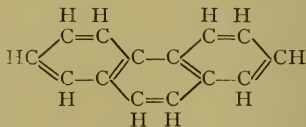
Naphthalene, anthracene and phenanthrene, it will be observed, closely resemble benzene in their general chemical behaviour; they are consequently represented by very similar symbols, the following being those usually employed:



Naphthalene.



Anthracene.



Phenanthrene.

The numerous cases of isomerism presented by the derivatives of naphthalene and anthracene are readily explained by the application of Kekulé's hypothesis of isomerism in the benzene series (pp. 127-132).

#### $C_nH_{2n-14}$ SERIES OF HYDROCARBONS.

The following hydrocarbons of this series are known:—

|                    |                | Melting-point.     | Boiling-point. |
|--------------------|----------------|--------------------|----------------|
| Diphenyl           | $C_{12}H_{10}$ | $60^{\circ}$       | $240^{\circ}$  |
| Acenaphthene       | $C_{12}H_{10}$ | $95^{\circ}$       | $268^{\circ}$  |
| Diphenylmethane    | $C_{13}H_{12}$ | $26^{\circ}\cdot5$ | $261^{\circ}$  |
| $\alpha$ -Ditolyl  | $C_{14}H_{14}$ | $121^{\circ}$      |                |
| $\beta$ -Ditolyl   |                | liquid             |                |
| Dibenzyl           |                | $52^{\circ}$       | $284^{\circ}$  |
| Benzyltoluene      |                | liquid             | $277^{\circ}$  |
| Benzylethylbenzene | $C_{15}H_{16}$ | liquid             | $294^{\circ}$  |
| Benzylmetaxylene   |                | liquid             | $295^{\circ}$  |
| Benzylparaxylene   |                | liquid             | $294^{\circ}$  |

Excepting acenaphthene all these act as saturated compounds, yielding substitution-derivatives when acted upon by bromine, nitric acid, &c., and not forming additive compounds.

DIPHENYL,  $C_{12}H_{10} = C_6H_5 \cdot C_6H_5$ , is produced—1. By passing benzene vapour through a red-hot tube:  $2C_6H_6 = C_{12}H_{10} + H_2$ . 2. By the action of sodium on monobromobenzene:  $2C_6H_5Br + Na_2 = 2NaBr + C_{12}H_{10}$ . Diphenyl crystallises in beautiful white iridescent nacreous scales which melt at  $70^{\circ}$ ; it is converted into benzoic acid on oxidation.

DITOLYL,  $C_{14}H_{14} = CH_3 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_3$ .—The two isomeric modifications are obtained by the action of sodium on the two isomeric monobromotoluenes (p. 125), the  $\alpha$ -modification being formed from the crystalline bromotoluene.

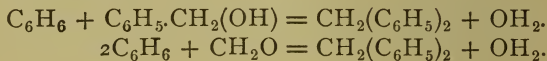
DIBENZYL,  $C_{14}H_{14} = C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$ , metameric with ditolyl, is prepared by acting upon benzylic chloride with sodium.

DIPHENYLMETHANE (*Benzylbenzene*),  $C_6H_5 \cdot CH_2 \cdot C_6H_5 = C_{13}H_{12}$ .—Benzylic chloride has but slight action on benzene at temperatures below  $100^{\circ}$ , but if finely divided zinc or copper be added, and the mixture gently heated, reaction takes place readily, hydrochloric acid is evolved, and diphenylmethane is formed, together with products of higher boiling-point not yet examined. The reaction which occurs may be formulated thus:  $C_6H_6 + C_7H_7Cl = HCl + C_{13}H_{12}$ .

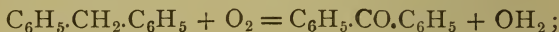


A certain amount of the metallic chloride is first formed, and recent experiments of Friedel and Crafts show that this, and not the metal, is the active agent, but the nature of its influence is obscure. Aluminic chloride is a still more powerful agent in effecting this and similar reactions (comp. p. 126). Thus *triphenylmethane*,  $\text{CH}(\text{C}_6\text{H}_5)_3$ , is obtained by its action on a mixture of benzene and trichloromethane; and a mixture of tetrachloromethane and benzene yields *tetraphenylmethane*,  $\text{C}(\text{C}_6\text{H}_5)_4$ .

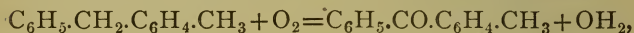
Diphenylmethane is also obtained by the action of sulphuric acid on a mixture of benzene with benzylic alcohol or formic aldehyde :<sup>1</sup>



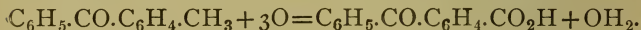
Diphenylmethane is converted on oxidation into the ketone, *benzophenone* :



the homologous benzyltoluene yields *methylbenzophenone* :



which on further oxidation yields *benzoylbenzoic acid* :

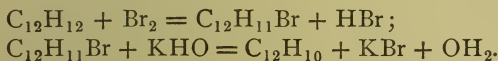


ACENAPHTENE,  $\text{C}_{12}\text{H}_{10}$ .—This hydrocarbon is contained in heavy coal-tar oils, and separates from the portion boiling between  $270^\circ$ – $300^\circ$  in large transparent prisms which melt at

<sup>1</sup> The various methods of obtaining diphenylmethane (and its homologues) afford most striking examples of the fact that a reaction possible between two bodies often does not take place until a third is introduced having a tendency to combine with, or be acted upon by, one of the products of that reaction. Thus no change occurs when benzene and benzylic alcohol are mixed until sulphuric is added, which then induces reaction apparently in virtue of the tendency which it has to enter into combination with water—a product of the reaction.

95°. In chemical behaviour it differs entirely from the other members of the series. Thus it unites directly with bromine to form a crystalline hexbromide,  $C_{12}H_{10}Br_6$ ; it also combines with trinitrophenol forming the compound  $C_{12}H_{10}, C_6H_3(NO_2)_3O$ , which crystallises in orange-yellow needles.

Acenaphthene is formed on passing naphthalene vapour and ethylene gas through a heated porcelain tube:  $C_{10}H_8 + C_2H_4 = C_{12}H_{10} + H_2$ . Also by strongly heating ethylnaphthalene,  $C_{12}H_{12} = C_{12}H_{10} + H_2$ ; or by the action of potassic hydrate on the first product of the action of bromine at 180° on ethylnaphthalene:



These reactions show that acenaphthene bears somewhat the same relation to ethylnaphthalene that cinnamene bears to ethylbenzene, or ethylene to ethane. On oxidation it is converted into naphthalic acid:  $C_{12}H_8O_4 = C_{10}H_6(CO_2H)_2$ , which on distillation with lime yields naphthalene.

## CHAPTER VI.

### ALCOHOLS.

By virtue of their modes of formation, the alcohols may be regarded as a class of bodies derived from the hydrocarbons by the substitution of hydrogen in the latter by the monad radicle hydroxyl, (OH). They may be termed *monohydric*, *dihydric*, *trihydric*, &c., according to the number of units of hydrogen thus supposed replaced in the parent hydrocarbon.

$C_nH_{2n+1}.OH$ , OR ETHYLIC SERIES OF MONOHYDRIC ALCOHOLS.

The alcohols of this series are derivatives of the paraffins; the following terms are known:—

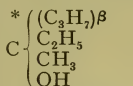
|                             |   |   |   |   |                                        |
|-----------------------------|---|---|---|---|----------------------------------------|
| Methylic alcohol            | . | . | . | . | $\text{CH}_3.\text{OH}$                |
| Ethylic                     | „ | . | . | . | $\text{C}_2\text{H}_5.\text{OH}$       |
| Propylic                    | „ | . | . | . | $\text{C}_3\text{H}_7.\text{OH}$       |
| Tetrylic or butylic alcohol | . | . | . | . | $\text{C}_4\text{H}_9.\text{OH}$       |
| Pentylic or amylic          | „ | . | . | . | $\text{C}_5\text{H}_{11}.\text{OH}$    |
| Hexylic alcohol             | . | . | . | . | $\text{C}_6\text{H}_{13}.\text{OH}$    |
| Heptylic                    | „ | . | . | . | $\text{C}_7\text{H}_{15}.\text{OH}$    |
| Octylic                     | „ | . | . | . | $\text{C}_8\text{H}_{17}.\text{OH}$    |
| Nonylic                     | „ | . | . | . | $\text{C}_9\text{H}_{19}.\text{OH}$    |
| Cetylic                     | „ | . | . | . | $\text{C}_{16}\text{H}_{33}.\text{OH}$ |
| Cerotic                     | „ | . | . | . | $\text{C}_{27}\text{H}_{55}.\text{OH}$ |
| Melissic                    | „ | . | . | . | $\text{C}_{30}\text{H}_{61}.\text{OH}$ |

The isomeric alcohols of the series, of which a considerable number exist, are divisible into the three groups of *primary*, *secondary*, and *tertiary* alcohols. Each of these groups is especially characterised and distinguished from the others by the behaviour on oxidation ; moreover the boiling points of the primary alcohols are always higher than those of the corresponding secondary, and the boiling points of the latter higher than those of the corresponding tertiary alcohols.

A systematic descriptive nomenclature for these alcohols has been proposed by Professor Kolbe, who applies to them the generic name of *carbinols*. The first term, methylic alcohol, is called *carbinol*, and the homologous alcohols are regarded as derived from it by the replacement of hydrogen by monad radicles of the form  $\text{C}_n\text{H}_{2n+1}$  ; thus ethylic alcohol is methylcarbinol— $\text{CH}_3.\text{CH}_2.\text{OH}$ , propylic alcohol is ethylcarbinol— $\text{C}_2\text{H}_5.\text{CH}_2\text{OH}$ , &c. Those alcohols which, by reason of their modes of formation, may be regarded as derived from carbinol by the substitution of only one unit of hydrogen in it, by a monad group of the form  $\text{C}_n\text{H}_{2n+1}$ , are termed primary alcohols ; if the replacement occur twice, a secondary alcohol is produced ; finally, if all three units of hydrogen in carbinol are replaced by three

# NORMAL TERTIARY.

## TERTIARY HEPTYLIC ALCOHOLS



Methylethyl-  
isopropylcarbinol  
B.-P. 124°-127°



Dimethyltertiary-  
butylcarbinol  
B.-P. 132°



Trimethylcarbinol  
B.-P. 82°·5



Ethyltrimethylcarbinol  
B.-P. 102°

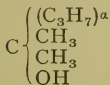


3

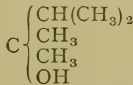
carbinol  
B.-P. 50°·5



Diethylmethylcarbinol  
B.-P. 119°-121°



Propyldimethyl-  
carbinol  
B.-P. 114°-117°



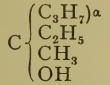
Isopropyldimethyl-  
carbinol  
B.-P. 112°-113°



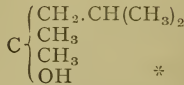
isopropylcarbinol  
P. 132°



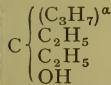
Triethylcarbinol  
B.-P. 140°-142°



Methylethyl-  
propylcarbinol  
B.-P. 135°-138°



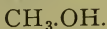
Isotetryldimethylcar-  
binol  
B.-P. 123°-132°



Propyldiethylcarbinol  
(Decomposes partially  
on distillation)

| NORMAL PRIMARY.                                                                                                                                                    | PRIMARY.                                                                                                                    | ISOSECONDARY.                                                                                                                         | NORMAL TERTIARY.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{CH}_3(\text{OH})$<br>Carbinol<br>B.-P. 66°<br><br>$(\text{CH}_3)_2\text{CH}_2(\text{OH})$<br>Methylcarbinol<br>B.-P. 78°-4                                  |                                                                                                                             |                                                                                                                                       | <div data-bbox="1323 160 1605 305" style="border: 1px solid black; padding: 5px;">           TERTIARY HEPTYLIC ALCOHOLS<br/>           * <math>(\text{C}_2\text{H}_5)_3\text{C}</math><br/> <math>\text{C} \begin{cases} \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{OH} \end{cases}</math><br/>           Methyl-ethyl-<br/>isopropylcarbinol<br/>B.-P. 124°-127°<br/> <math>\text{C} \begin{cases} \text{C}(\text{C}_2\text{H}_5)_2 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{OH} \end{cases}</math><br/>           Dimethyl-tertiary-<br/>butylcarbinol<br/>B.-P. 132°         </div> |
| PROPYLIC SERIES, $\text{C}_3\text{H}_7(\text{OH})$ :—<br><br>$(\text{C}_2\text{H}_5)_2\text{CH}_2(\text{OH})$<br>Ethylcarbinol<br>B.-P. 97°-98°                    |                                                                                                                             | $\text{CH} \begin{cases} \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Ethylmethylcarbinol<br>B.-P. 83°            |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| TETRYLIC OR BUTYLIC SERIES, $\text{C}_4\text{H}_9(\text{OH})$ :—<br><br>$(\text{C}_2\text{H}_5)_3\text{C}$<br>Propylcarbinol<br>B.-P. 116°                         | $\text{CH}(\text{CH}_3)_2\text{CH}_2(\text{OH})$<br>Isopropylcarbinol<br>B.-P. 109°                                         | $\text{CH} \begin{cases} \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Ethylmethylcarbinol<br>B.-P. 99°            | $\text{C} \begin{cases} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Trimethylcarbinol<br>B.-P. 82°-5                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| PENTYLIC OR AMYLIC SERIES, $\text{C}_5\text{H}_{11}(\text{OH})$ :—<br><br>$(\text{C}_4\text{H}_9)_2\text{CH}_2(\text{OH})$<br>Teteryl(butyl)carbinol<br>B.-P. 137° | $(\text{C}_4\text{H}_9)_2\text{CH}_2(\text{OH})$<br>Isobutylcarbinol<br>B.-P. 131°                                          | $\text{CH} \begin{cases} (\text{C}_3\text{H}_7)^a \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Propylmethylcarbinol<br>B.-P. 118°-120° | $\text{C} \begin{cases} \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Ethylmethylcarbinol<br>B.-P. 102°                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| HEXYLIC SERIES, $\text{C}_6\text{H}_{13}(\text{OH})$ :—<br><br>$(\text{C}_2\text{H}_5)_3\text{C}$<br>Pentylcarbinol<br>B.-P. 157°                                  | $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{OH})$<br>Isopentylcarbinol<br>B.-P. 150° (about)           | $\text{CH} \begin{cases} (\text{C}_3\text{H}_7)^a \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Teterylmethylcarbinol<br>B.-P. 137°     | $\text{C} \begin{cases} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Diethylmethylcarbinol<br>B.-P. 119°-121°                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| HEPTYLIC SERIES, $\text{C}_7\text{H}_{15}(\text{OH})$ :—<br><br>$(\text{C}_6\text{H}_{13})_2\text{CH}_2(\text{OH})$<br>Hexylcarbinol<br>B.-P. 175°-5-177°-5        | $\text{CH}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{OH})$<br>Isohexylcarbinol<br>B.-P. 165° (about) | $\text{CH} \begin{cases} (\text{C}_3\text{H}_7)^a \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Propylmethylcarbinol<br>B.-P. 160°-162° | $\text{C} \begin{cases} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Triethylcarbinol<br>B.-P. 140°-142°                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
| OCTYLIC SERIES, $\text{C}_8\text{H}_{17}(\text{OH})$ :—<br><br>$(\text{C}_7\text{H}_{15})_2\text{CH}_2(\text{OH})$<br>Heptylcarbinol<br>B.-P. 196°-197°            |                                                                                                                             | $\text{CH} \begin{cases} (\text{C}_3\text{H}_7)^a \\ \text{CH}_3 \\ \text{OH} \end{cases}$<br>Hexylmethylcarbinol<br>B.-P. 181°       | $\text{C} \begin{cases} (\text{C}_3\text{H}_7)^a \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{OH} \end{cases}$<br>Propyldiethylcarbinol<br>(Decomposes partially on distillation)                                                                                                                                                                                                                                                                                                                                                                                                         |

such groups, a tertiary alcohol results from the action of monohydric alcohols of the ethylic series, and is represented by the following general expression:



Carbinol.



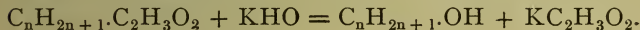
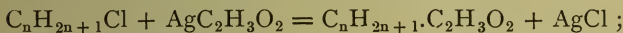
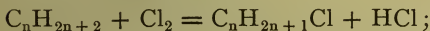
Primary Carbinol.

Secondary Carbinol.

Tertiary Carbinol.

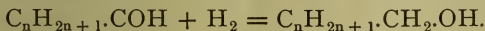
# GENERAL METHODS OF FORMATION OF THE ALCOHOLS OF THE $\text{C}_n\text{H}_{2n+1}.\text{OH}$ SERIES.

*Normal Primary Alcohols*,  $\text{C}(\text{C}_n\text{H}_{2n+1})\text{H}_2.\text{OH}$ .—I. The normal primary paraffins are converted by the action of chlorine into monochlorinated derivatives; the monochlorinated paraffins thus produced are acted upon by argentic or potassic acetate, and the ethereal salts so formed then saponified by potassic hydrate, whereby the required alcohols and potassic acetate are produced:



It is to be remembered, however, that two isomeric monochlorinated paraffins are usually produced simultaneously by the action of chlorine on a normal primary paraffin (p. 85). Only one of these—that of higher boiling-point—yields a normal primary alcohol; that of lower boiling-point yields a normal secondary alcohol.

2. The action of nascent hydrogen (sodium amalgam) on the normal primary aldehydes of the acetic series:



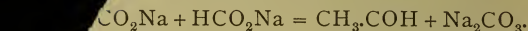
This method affords the means of ascending the series of normal primary alcohols. Thus methylic alcohol may be obtained from formic aldehyde:  $\text{HCOH} + \text{H}_2 = \text{CH}_3.\text{OH}$ , and may then be converted into iodomethane,  $\text{CH}_3\text{I}$ , by the action of hydriodic acid, from which, by the action of potassic



...e,  $\text{CH}_3\cdot\text{CN}$ , is obtained. Cyanomethane is converted into acetic acid by oxidation with sodic hydrate into sodic acetate:



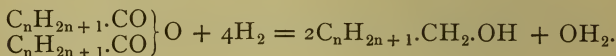
...ation with sodic formate yields acetic aldehyde:



...y the action of nascent hydrogen on acetic aldehyde, ... alcohol is obtained :  $\text{CH}_3\cdot\text{COH} + \text{H}_2 = \text{CH}_3\cdot\text{CH}_2\cdot\text{OH}$ .

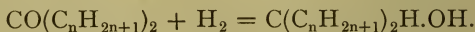
...e manner, ethylic alcohol may be converted into primary ...ylic alcohol, and this again into primary butylic alcohol, &c.

3. The action of nascent hydrogen on the anhydrides of the normal primary acids of the acetic series :



*Isoprimary Alcohols*.—These are isomeric with the normal-primary alcohols, than which they invariably possess lower boiling-points. They are produced by the action of nascent hydrogen on the isoprimary aldehydes of the  $\text{C}_n\text{H}_{2n+1}\text{COH}$  series. Several are obtained as by-products in the manufacture of ordinary alcohol by fermentation.

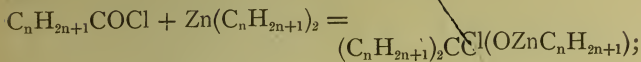
*Normal Secondary Alcohols*,  $\text{C}(\text{C}_n\text{H}_{2n+1})_2\text{H}\cdot\text{OH}$ .—These are prepared by the action of nascent hydrogen on the normal primary ketones of the form  $\text{CO}(\text{C}_n\text{H}_{2n+1})_2$  :



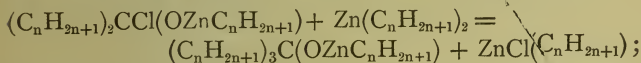
The ketones isomeric with the normal primary ketones yield isosecondary alcohols. Normal secondary alcohols are also formed from the normal primary paraffins (p. 145).

*Tertiary Alcohols*,  $\text{C}(\text{C}_n\text{H}_{2n+1})_3\cdot\text{OH}$ .—These are obtained by the action of the zinc organo-metallic compounds on the acid chlorides of the form  $\text{C}_n\text{H}_{2n+1}\cdot\text{COCl}$ , the product being allowed to stand some time and then treated with water. A

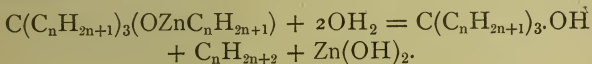
series of reactions occur, the following being probably the first:



this compound, however, is further slowly acted upon:



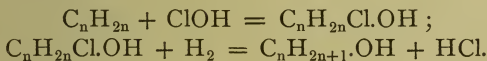
and in the last stage the compound thus formed is converted by the water into a tertiary alcohol, a paraffin, and zinc hydrate:



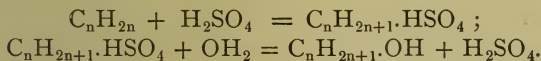
By employing a different zinc compound to effect the second reaction, alcohols containing three different radicles may be formed, such as methylethylpropylcarbinol (see table).

Other general methods of preparing alcohols of the  $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$  series, but which sometimes give rise to the formation of primary, sometimes to the formation of secondary or tertiary alcohols, are the following:—

1. The action of nascent hydrogen on the chlorinated alcohols formed by the direct union of the olefines with hypochlorous acid:



2. The action of water on the products of the direct union of the olefines with concentrated sulphuric acid:



3. The action of potassic or argentic acetate on the moniodo-paraffins obtained by the union of the olefines with hydriodic acid, and subsequent saponification of the ethereal salts thus formed by potassic hydrate.

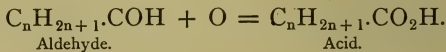
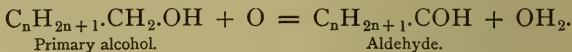
4. The decomposition of the nitrites of the amine bases by application of heat to their slightly acidulated solutions :



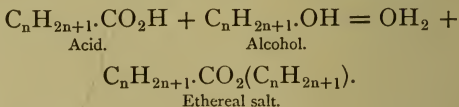
GENERAL PROPERTIES OF THE ALCOHOLS OF THE  
 $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$  SERIES.

The first nine members of the series are colourless liquids at ordinary temperatures ;<sup>1</sup> methylic, ethylic, and propylic alcohols are extremely mobile fluids, soluble in water in all proportions, but the higher members are more or less oily, the viscosity increasing, and the solubility in water rapidly decreasing as the series is ascended ; the specific gravity also increases as the alcohols become more complex. They all possess more or less characteristic odours.

*Behaviour on Oxidation.—Primary Alcohols.*—The oxidation of the primary alcohols occurs at two stages: at the first, an aldehyde is produced, which on further oxidation is converted into an acid of the acetic series containing *the same number* of units of carbon as the alcohol oxidised :



In most cases also a portion of the acid reacts at the moment of formation on the alcohol under oxidation, to form an ethereal salt (a so-called compound ether), thus :

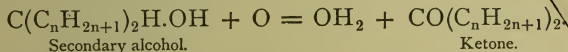


The primary alcohols therefore may furnish three distinct

<sup>1</sup> Trimethylcarbinol, and a few other tertiary alcohols are crystalline solids.

products on oxidation ; the relative proportions in which these are obtained depends entirely on the conditions of experiment : on the temperature, on the nature of the oxidiser employed, on the amount of water present, and also probably on the nature of the alcohol.

*Secondary Alcohols.*—Secondary alcohols are invariably converted into ketones, and by the continued action of the oxidiser, these latter are resolved into one or more acids of the acetic series, containing *fewer* units of carbon than the alcohol oxidised (see ketones) :



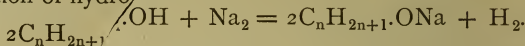
*Tertiary Alcohols.*—A number of these are resolved on oxidation into a ketone and an acid of the acetic series :



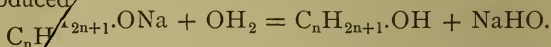
This is in all probability the normal reaction, although the formation of a ketone as first product has not been demonstrated in all cases ; but that this should have sometimes escaped observation is not surprising, since the ketones are themselves readily oxidised. The sole product obtained from certain of the tertiary alcohols has been, in fact, a mixture of acids of the acetic series (compare p. 216).

The three classes of isomeric alcohols are therefore readily distinguished by the behaviour on oxidation, for whilst the primary alcohols yield an aldehyde, and (as final product) an acid containing the same number of units of carbon as the parent alcohol, the secondary alcohols yield a ketone containing the same number of units of carbon as the alcohol oxidised, which is resolved, on further oxidation, into an acid (or mixture of acids) containing fewer units of carbon than itself, and the tertiary alcohols either furnish a ketone *plus an acid*, or a mixture of acids, of the acetic series.

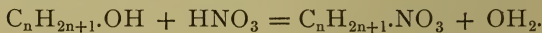
*Other Reactions of the Alcohols of the  $C_nH_{2n+1}.OH$  Series.*—  
They are readily attacked by potassium or sodium with evolution of hydrogen and formation of metallic derivatives :



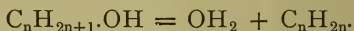
These bodies are decomposed by water: the alcohol is reproduced, and a metallic hydrate is formed :



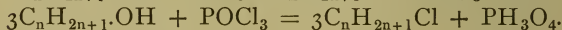
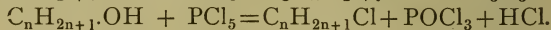
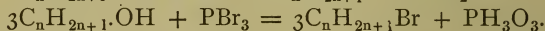
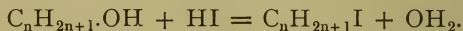
2. They react with nearly all the oxacids to form ethereal salts (compound ethers), e.g. :



3. By the action of various dehydrating agents, such as zincic chloride, sulphuric acid, &c., at moderate temperatures on these alcohols, the elements of water are withdrawn, and the corresponding olefines obtained :



4. They are invariably converted by the action of the haloid acids, or of the haloid phosphorus compounds, into mono-haloid derivatives of the corresponding paraffins :

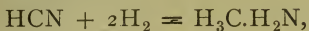


5. On distilling them with phosphoric pentasulphide, the corresponding thio-alcohols (mercaptans) are produced :



METHYLIC ALCOHOL or CARBINOL (*Wood or Pyroxylic Spirit*),  $CH_4O = CH_3.OH$ .—No isomeric modifications of this, the first member of the series, are known. It has been prepared by the first and second general methods from methane and formic aldehyde, and by the following special methods.

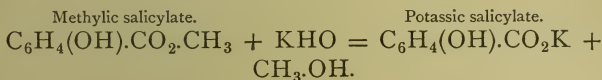
1. Hydrocyanic acid is converted by the action of nascent hydrogen into methylamine :



and the nitrite of this base is decomposed by boiling its acidulated aqueous solution :



2. By saponification of wintergreen oil (the essential oil of *Gaultheria procumbens*) with potassic hydrate:



The chief source of methylic alcohol, however, is crude wood vinegar, the watery liquid obtained by destructive distillation of wood. Hence the name *wood* or *pyroxylic spirit*, which is often applied to this alcohol.

The watery liquid is distilled, and the more volatile portion which first passes over is collected apart; this distillate is neutralised with slaked lime, the clear liquid is separated from the excess of lime, and from the oil which floats on its surface, and is redistilled, and the product several times rectified over quicklime, at the heat of the water-bath. Pure alcohol is obtained from this comparatively crude product, by dissolving calcic chloride in it, with which it unites to form a crystalline compound,  $\text{CaCl}_2.2\text{CH}_4\text{O}$ . After pouring off any oily liquid from the solid cake which forms, the latter is heated for some time on the water-bath, in a current of carbonic anhydride, or is strongly pressed between folds of bibulous paper; finally, water is added (which decomposes the compound  $\text{CaCl}_2.2\text{CH}_4\text{O}$ ) and the alcohol distilled off; if necessary, this is again converted into the solid compound, &c. The aqueous alcohol thus obtained is rendered anhydrous by rectifying, first over quick lime, and then over dehydrated cupric sulphate. The pure alcohol may also be obtained by converting the crude alcohol into methylic oxalate,  $\text{C}_2\text{O}_4(\text{CH}_3)_2$ , a solid substance which is readily purified

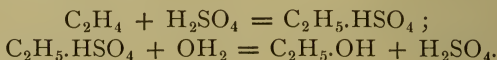


by recrystallisation, by distilling a mixture of equal parts of the alcohol, sulphuric acid and oxalic acid; the purified oxalate is then decomposed by water, the alcohol distilled off, &c.

Pure methylic alcohol closely resembles ordinary or ethylic alcohol in odour and taste, but the crude alcohol has an extremely offensive smell and taste. It possesses all the solvent properties of ordinary alcohol, and is therefore largely substituted for it in various industrial processes. It boils at about  $66^{\circ}$ .

*Methylated spirit* is a mixture of 90 per cent. ethylic alcohol (sp. gr. about  $\cdot 83$ ) with 10 per cent. partially purified wood spirit; this mixture may be employed for the greater number of purposes for which alcohol is ordinarily used, at the same time it cannot be separated into its constituents by distillation, and it is rendered quite unfit for consumption by the small admixture of impure wood spirit, in consequence of which it is allowed by the legislature to pass duty free.

ETHYLIC ALCOHOL, or METHYLCARBINOL (*Alcohol, Spirit of Wine*):  $C_2H_6O = C_2H_5.OH = CH_3.CH_2.OH$ .—Isomerides of this alcohol are also unknown. It has been prepared by the general methods from ethane, acetic aldehyde, and acetic anhydride, and by the four additional methods referred to on pp. 147–148. The greatest interest attaches to the formation of alcohol from ethylene, since ethylene may be prepared from acetylene, which is the only known hydrocarbon that can be obtained by the direct union of its elements. The synthesis is effected by combining the ethylene with sulphuric acid, and subsequently distilling the product—hydric ethylic sulphate, *sulphovinic acid*—with water:



The combination of ethylene with sulphuric acid takes place very slowly, it is therefore necessary to enclose the former,

together with a sufficiency of the latter, in a capacious glass flask, and to agitate violently for a considerable time.

On the large scale alcohol is always prepared by the fermentation of sugar. When a solution of cane-sugar, or grape-sugar (glucose— $C_6H_{12}O_6$ ) is mixed with beer yeast, a peculiar change, technically called *fermentation*, is induced, whereby the glucose is resolved into alcohol and carbonic anhydride:  $C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O$ . Cane-sugar is first converted into glucose by the assumption of water:  $C_{12}H_{22}O_{11} + OH_2 = 2C_6H_{12}O_6$ .

The spirit first obtained by distilling a fermented saccharine liquid is still largely diluted with water; by redistilling and collecting apart the first portions which pass over, a stronger spirit may be obtained, but, practically, one containing less than 13 or 14 per cent. of water is never prepared by rectification alone. *Rectified spirit of wine* of commerce (sp. gr. .835) has about this strength; *proof spirit* has a specific gravity of .9198 at  $15.5^\circ$  C. ( $60^\circ$  F.), and contains  $49\frac{1}{2}$  per cent. of real alcohol. Pure or *absolute* alcohol may be obtained from spirit of wine by allowing it to remain for some days in contact with freshly burnt lime, and then distilling it off by the heat of a water-bath; or the dehydration may be more rapidly effected by digesting the spirit, at its boiling-point, with the lime, in a retort connected with a condenser to prevent volatilisation and loss of alcohol.

Pure alcohol is a colourless, highly mobile liquid of pungent and agreeable taste and odour; it has a specific gravity of .7938 at  $15.5^\circ$  C. It is very inflammable and burns with a pale-bluish, scarcely luminous, smokeless flame. Alcohol boils at  $78.4^\circ$  under a pressure of 760 mm. of mercury; it has never yet been frozen, hence its employment in the manufacture of thermometers to indicate very low temperatures. It is an extremely hygroscopic substance, attracting moisture with great avidity; it is miscible with water in all proportions, and in the act of dilution heat is evolved, and contraction of volume occurs.

A very careful series of determinations of the specific gravity, at various temperatures, of solutions containing known quantities of alcohol and water, both by volume and by weight, have been made, and from these tables have been constructed, which are to be found in all the larger works on chemistry. In practice, the percentage of alcohol in a given aqueous solution is always thus ascertained by determining its specific gravity at a known temperature, and then referring to such a table of strengths. Hydrometers are also constructed with scales marking directly the percentage of alcohol by volume, and sometimes also by weight, of the spirit in which they are immersed. Such instruments are known as *alcoholometers*.

Alcohol enters into combination with certain salts to form crystalline compounds termed *alcoholates*, which are salts containing alcohol in the place of water of crystallisation. Such are the following :



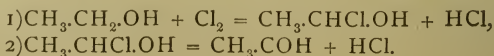
These alcoholates are decomposed by water.

Potassium and sodium dissolve in alcohol with evolution of hydrogen :  $2\text{C}_2\text{H}_5\cdot\text{OH} + \text{Na}_2 = 2\text{C}_2\text{H}_5\cdot\text{ONa} + \text{H}_2$ . By employing an excess of alcohol, sodic ethylate may be obtained crystallised, combined with alcohol in the proportions indicated by the formula  $\text{C}_2\text{H}_5\cdot\text{ONa}, 3\text{C}_2\text{H}_6\text{O}$ .

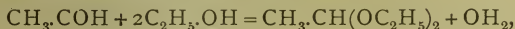
On oxidation, alcohol is converted into aldehyde,  $\text{C}_2\text{H}_4\text{O}$ , and finally into acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ .

Chlorine is rapidly absorbed by anhydrous alcohol with considerable evolution of heat ; the chief end-product is *chloral alcoholate*, but a number of intermediate and also of secondary products are obtained, the formation of which may be traced as follows :—

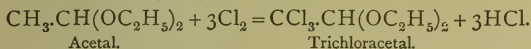
By the first action of the chlorine, a portion of the alcohol is converted into *aldehyde*, and probably this conversion occurs at two stages, as represented by the following equations :



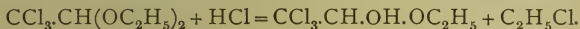
The aldehyde thus formed unites, partially at least, with a further portion of alcohol, forming *acetal* :



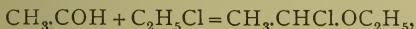
which by the continued action of the chlorine is successively converted into *mono*-, *di*-, and *trichloracetal* :



Finally, the latter is acted upon by the hydrochloric acid generated in the previous reactions, (or in part perhaps by water) and converted into chloral alcoholate and monochlorethane :



Simultaneously with these occur the following reactions. The hydrochloric acid which results from the first action of the chlorine on the alcohol partially converts the latter into monochlorethane :  $\text{C}_2\text{H}_5\cdot\text{OH} + \text{HCl} = \text{C}_2\text{H}_5\text{Cl} + \text{OH}_2$ , and this at the moment of formation combines with a portion of the aldehyde produced, and yields *monochlorinated ethylic ether* :



which, by the continued action of the chlorine, is ultimately converted into tetrachlorinated ether,  $\text{CCl}_3\cdot\text{CHCl}\cdot\text{OC}_2\text{H}_5$ . The product of the action of chlorine on alcohol also contains some chloral hydrate,  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ , formed either by the action of hydrochloric acid or water (or more probably of both) on the chloral alcoholate, or by the action of water [which is itself produced in the reaction] on the tetrachlorinated ether.

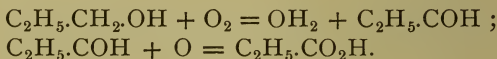
The secondary products consist mainly of chlorinated derivatives of monochlorethane,  $\text{C}_2\text{H}_5\text{Cl}$ .

The product obtained in the preparation of chloral hydrate by the action of chlorine on alcohol containing more or less water, is therefore extremely complex, but since chloral alcoholate and tetrachlorinated ether are readily resolved into chloral and alcohol, or chloral and monochlorethane, by the action of concentrated sulphuric acid, pure chloral hydrate is readily obtained by first thus separating the chloral, and subsequently converting it into the hydrate by mixing it with water. It is necessary at first to cool the alcohol, but afterwards the action must be assisted by the application of heat.

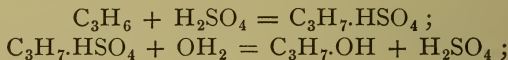
PROPYLIC ALCOHOL  $C_3H_7.OH$ .—Two isomeric modifications of this alcohol are known, distinguished as *normal propylic alcohol* or *ethylcarbinol*,  $C_2H_5.CH_2.OH$ , and *isopropylic alcohol* or *dimethylcarbinol*,  $C(CH_3)_2H.OH$ . The former of these is a primary and the latter a secondary alcohol.

*Normal propylic alcohol* has been isolated from the mixture of alcohols produced on fermentation of various kinds of grain, and it is especially abundant in the spirit obtained on distillation of cider. It has been synthesised by all the general methods mentioned on pp. 145–146.

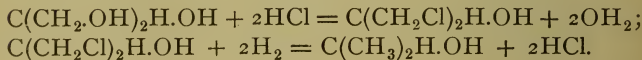
It is converted into propionic aldehyde and propionic acid on oxidation :



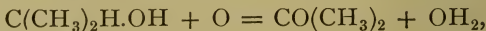
*Isopropylic alcohol* is also produced, it is said, on fermentation of grain. It is obtained from acetone by the action of nascent hydrogen :  $CO(CH_3)_2 + H_2 = C(CH_3)_2H.OH$  ; from propylene,  $C_3H_6$ , by combining it with sulphuric acid and distilling the resulting compound with water :



and by the action of nascent hydrogen on *dichlorhydrin*, a product of the action of hydrochloric acid on glycerin :



Isopropylic alcohol is converted into acetone on oxidation :



which by the continued action of the oxidiser is resolved into acetic acid, carbonic anhydride, and water :



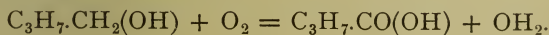
Isopropylic alcohol forms with water several hydrates of considerable stability ; it is impossible, for instance, to dehydrate it with anhydrous cupric sulphate, one of the most powerful desiccating agents at the chemist's disposal. One of these hydrates,  $2\text{C}_3\text{H}_8\text{O}, \text{OH}_2$ , has the same percentage composition and very nearly the same boiling-point as ethylic alcohol.

*Relation of Propylic to Isopropylic Alcohol.*—On the one hand the primary alcohol is convertible into propylene,  $\text{C}_3\text{H}_6$ , from which, it has been shown, isopropylic alcohol is obtainable ; on the other the  $\beta$ -iodopropane formed on treating isopropylic alcohol with hydriodic acid is converted into propane by the action of nascent hydrogen, and this propane may be changed by the first general method (p. 145) into normal propylic alcohol.

**TETRYLIC or BUTYLIC ALCOHOL,  $\text{C}_4\text{H}_9\text{OH}$ .**—Four isomeric modifications of this alcohol exist, namely :—

|                                 |                                                           |       |
|---------------------------------|-----------------------------------------------------------|-------|
| Normal primary butylic alcohol. |                                                           | B.-P. |
| Propylcarbinol                  | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2(\text{OH})$ | 116°  |
| Iso-primary butylic alcohol.    |                                                           |       |
| Isopropylcarbinol               | $\text{CH}(\text{CH}_3)_2\text{CH}_2(\text{OH})$          | 109°  |
| Secondary butylic alcohol.      |                                                           |       |
| Methylethylcarbinol             | $\text{CH}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{OH})$ | 99°   |
| Tertiary butylic alcohol.       |                                                           |       |
| Trimethylcarbinol               | $\text{C}(\text{CH}_3)_3(\text{OH})$                      | 82°·5 |

The normal primary alcohol has been obtained by the three general methods (pp. 145-146). It yields normal butyric acid on oxidation :

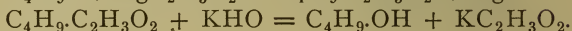
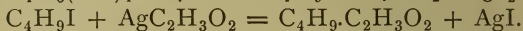
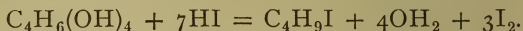


Isoprimary butylic alcohol is present in considerable quantity in the fermentation-product of sugar-beet molasses, from which it may be isolated by careful fractional distillation. It is converted into isobutyric acid on oxidation :

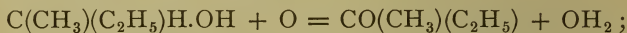




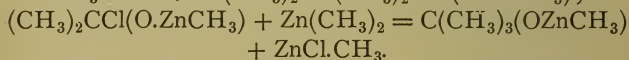
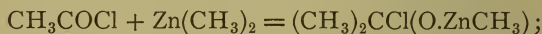
Secondary butylic alcohol has been obtained by saponifying the acetate formed from the iodotetrane which is produced by distilling *erythrite* with hydriodic acid :



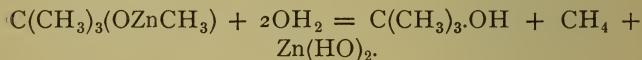
On oxidation it is converted into *methylethylketone*, which on continued oxidation yields acetic acid :



Tertiary butylic alcohol is prepared by slowly adding acetic chloride to well-cooled zincic methide, and adding water to the product *after it has stood several days*. The first action probably takes place in two stages, thus :

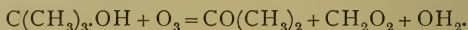


The subsequent action of water is represented by the equation :



The oxidation-products of trimethylcarbinol are *isobutyric*, acetic and formic acid, acetone, isobutylene, carbonic anhydride, and water.

The primary reaction doubtless consists in the formation of acetone and formic acid :



The former is rapidly further oxidised to acetic acid, &c., and the latter to carbonic anhydride and water. The isobutylene is the product of a secondary reaction, whereby the alcohol is resolved into isobutylene and water :  $\text{C}_4\text{H}_9\cdot\text{OH} = \text{OH}_2 + \text{C}_4\text{H}_8$ ,

and which is probably the result of the dehydrating action exercised by the sulphuric acid employed in the oxidising mixture. It is difficult to account satisfactorily for the formation of isobutyric acid; it must be regarded as the product of an isomeric change which cannot at present be traced.

*Relations of the Isomeric Butylic Alcohols.*

1. If *normal primary butylic alcohol* be converted into butylamine,  $C_4H_9.H_2N$ , and the nitrite of this base be decomposed by boiling its acidulated aqueous solution, *isoprimary butylic alcohol* is obtained.

2. By a repetition of this process on the alcohol thus formed, it is converted into *tertiary butylic alcohol*.

3.  $\alpha$ -Iodotetrane obtained by the action of hydriodic acid on *normal butylic alcohol* yields on treatment with an alcoholic solution of potassic hydrate, a butylene which combines readily with hydriodic acid, but the product ( $\gamma$ -iodotetrane)<sup>1</sup> is isomeric with the iodotetrane used at starting, being convertible by the ordinary method into *secondary butylic alcohol*.

4. Isoprimary butylic alcohol may be converted into the tertiary alcohol by a variety of methods; thus, for example, the  $\beta$ -iodotetrane obtained from it by the action of hydriodic acid yields a butylene on treatment with an alcoholic solution of potassic hydrate which combines readily with concentrated sulphuric acid and with hydriodic acid; if the product with sulphuric acid be distilled with water, or if the product with hydriodic acid be caused to act upon argentic acetate, and the resulting acetate be saponified by potassic hydrate, tertiary butylic alcohol results.

5. The butylene obtained by heating tertiary butylic alcohol with hydriodic acid, and decomposing the resulting  $\delta$ -iodotetrane by potassic hydrate, combines directly with

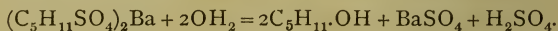
<sup>1</sup>  $\alpha$ -Iodotetrane boils at  $129^{\circ}.5$ ;  $\beta$  iodotetrane at  $122^{\circ}.5$ ;  $\gamma$ -iodotetrane at  $116^{\circ}$ – $120^{\circ}$ ;  $\delta$ -iodotetrane at  $98^{\circ}$ – $99^{\circ}$ .

hypochlorous acid ; the resulting monochlorinated butylic alcohol is converted into isoprimary butylic alcohol by the action of nascent hydrogen.

PENTYLIC OR AMYLIC ALCOHOL,  $C_5H_{11}.OH$ .—We are at present acquainted with six isomeric modifications of this alcohol, four of which are obtained by purely synthetic methods, and are comparatively little known.

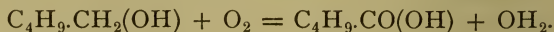
*Isoprimary amylic alcohol* or *isobutylcarbinol* is the chief constituent of the fusel oil<sup>1</sup> obtained in the manufacture of spirit by fermentation of grain and potatoes. Ordinary fusel oil, however, contains two isomeric modifications, which scarcely differ (if at all) in chemical properties, but are distinguished by their behaviour towards polarised light, the one having no action, the other rotating the ray considerably to the left. The boiling-points of these two alcohols differ by at most  $2^\circ$ , that of the inactive being  $129^\circ$ – $130^\circ$ , that of the active about  $128^\circ$ .

They are separated by acting upon the mixture with concentrated sulphuric acid, and converting the hydric amylic sulphates produced ( $C_5H_{11}.OH + H_2SO_4 = C_5H_{11}.HSO_4 + OH_2$ ) into baric salts. The baric salt of the product from the active alcohol being about  $2\frac{1}{2}$  times more soluble in water than the corresponding inactive derivative, the mixed salts may be separated by repeated recrystallisation, and the pure alcohols then obtained by distilling the pure baric salts with dilute sulphuric acid, &c. :



It is said that the active alcohol becomes optically inactive when repeatedly distilled over sodic hydrate.

Both modifications yield a *valeric* acid on oxidation :



The acid from the inactive alcohol is optically inactive ; that from the active alcohol is strongly dextrorotary. The

<sup>1</sup> Fusel oil is the portion, of higher boiling-point than ethylic alcohol, separated from the crude product of fermentation by distillation.

two acids are further distinguished by the fact that the former yields a crystalline baric salt, whereas the baric salt prepared from the active acid cannot be obtained in the crystalline condition.

The inactive alcohol is undoubtedly correctly represented by the formula  $\text{CH}(\text{CH}_3)_2.\text{CH}_2.\text{CH}_2(\text{OH})$ , since the valeric acid which it yields on oxidation may be obtained from isopropylcarbinol (see valeric acid). The active alcohol has the formula  $\text{C}_2\text{H}_5.\text{CH}(\text{CH}_3).\text{CH}_2(\text{OH})$ .

*Cetylic Alcohol*,  $\text{C}_{16}\text{H}_{33}.\text{OH}$ ; *Cerotic* or *Cerylic Alcohol*,  $\text{C}_{27}\text{H}_{55}.\text{OH}$ ; and *Melissic Alcohol*,  $\text{C}_{30}\text{H}_{61}.\text{OH}$ , which are respectively obtained by saponifying spermaceti (cetylic palmitate), Chinese-wax (cerylic cerotate), and myricin (melissic palmitate)—the portion of common bees'-wax insoluble in boiling alcohol, are white crystalline substances. They exchange (OH) for Cl when acted upon by  $\text{PCl}_5$ , and yield the corresponding acids of the  $\text{C}_n\text{H}_{2n+1}.\text{CO}_2\text{H}$  series on oxidation; on distillation they are partially resolved into water and the corresponding olefine.

# $\text{C}_n\text{H}_{2n-1}.\text{OH}$ OR ALLYLIC SERIES OF MONOHYDRIC ALCOHOLS.

The alcohols of this series bear the same relation to the olefines that the alcohols of the ethylic series bear to the paraffins. The following are known :

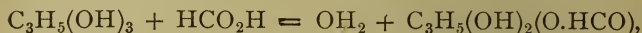
|                             |                                                                   |
|-----------------------------|-------------------------------------------------------------------|
| Allylic alcohol . . . .     | $\text{CH}_2:\text{CH}.\text{CH}_2.\text{OH}$                     |
| Allyldimethylcarbinol . . . | $\text{C}_3\text{H}_5.\text{C}(\text{CH}_3)_2.\text{OH}$          |
| Allyldiethylcarbinol . . .  | $\text{C}_3\text{H}_5.\text{C}(\text{C}_2\text{H}_5)_2.\text{OH}$ |
| Allyldipropylcarbinol . . . | $\text{C}_2\text{H}_5.\text{C}(\text{C}_3\text{H}_7)_2.\text{OH}$ |

ALLYLIC ALCOHOL,  $\text{C}_3\text{H}_5.\text{OH} = \text{CH}_2.\text{CH}:\text{CH}_2(\text{OH})$ .—

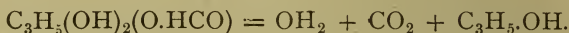
*Preparation*.—1. From allylic iodide,  $\text{C}_3\text{H}_5\text{I}$ , the product of the action of phosphorus iodide on glycerin (see glycerin).

The iodide is converted into allylic oxalate,  $(\text{C}_3\text{H}_5)_2\text{C}_2\text{O}_4$ , by acting upon it with argentic oxalate,  $\text{Ag}_2\text{C}_2\text{O}_4$ , and the oxalate decomposed by ammonia, whereby allylic alcohol and oxamide are produced :  $(\text{C}_3\text{H}_5)_2\text{C}_2\text{O}_4 + 2\text{NH}_3 = 2\text{C}_3\text{H}_5.\text{OH} + \text{C}_2\text{O}_2\text{N}_2\text{H}_4$ .

2. By heating glycerin with oxalic acid. In the first place the oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is resolved on heating into carbonic anhydride and formic acid; the latter then reacts on the glycerin to produce *monoformin*:



which, on further heating, splits up into water, carbonic anhydride, and allylic alcohol:



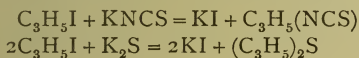
The mixture of four parts of glycerin and one part of oxalic acid is heated in a retort provided with a thermometer and connected with a condenser, the receiver being changed when the temperature rises to  $195^\circ$ , and the distillation continued from that point to  $260^\circ$ . When ordinary commercial oxalic acid is employed, a small quantity (about one per cent.) of ammoniac chloride is added. The distillate, a mixture of aqueous allylic alcohol and other products, is rectified, digested with potassic hydrate, distilled, dried over potassic carbonate, again digested with potassic hydrate, redistilled, and freed from the last traces of water by rectification over anhydrous baryta. A fair yield of the alcohol is obtained by this method.

Allylic alcohol is a colourless liquid of sharp, irritating odour, miscible in all proportions with water; sp. gr.  $\cdot 8709$  at  $0^\circ$ ; boiling-point  $96^\circ$ . It is not affected by nascent hydrogen (from sodium amalgam and water), but yields normal propylic alcohol, together with oxidation-products, when heated to  $150^\circ$  with potassic hydrate. On oxidation, allylic alcohol yields *acrolein*,  $\text{C}_2\text{H}_3.\text{COH}$ , formic acid, and carbonic anhydride. It exchanges (OH) for Cl, Br, I, &c.,<sup>1</sup> when acted upon by the haloid acids, or haloid phosphorus compounds, and reacts with sulphuric acid to form hydric

<sup>1</sup> The haloid derivatives so produced unite directly with the halogens and haloid acids to form haloid substitution-derivatives of the paraffin propane.

allylic sulphate,  $C_3H_5.HSO_4$ , thus resembling the alcohols of the ethylic series, from which it differs, however, in that it combines directly with chlorine and bromine, &c., to form such compounds as  $C_3H_5Cl_2(OH)$ ,  $C_3H_5Br_2(OH)$ , from which allylic alcohol is again obtained on submitting them to the action of nascent hydrogen.

*Mustard and Garlic Oils.*—Black mustard seed contains the potassic salt of an acid termed myronic acid, which is decomposed when the bruised seed is macerated for some hours with water, and on distilling the water an oil passes over with it. The volatile oil thus obtained has the composition of allylic sulphocyanate,  $C_3H_5(NCS)$ . Garlic, on the other hand, contains an offensive smelling oil of the composition of allylic sulphide,  $(C_3H_5)_2S$ . The substances of this composition prepared by the following synthetic reactions from allylic iodide :



are found identical in every respect with the natural products.

### $C_nH_{2n-3}.OH$ SERIES OF MONOHYDRIC ALCOHOLS.

The first member of this series, Propargylic alcohol,  $HC:C.CH_2(OH)$ , has been obtained by the action of potassic hydrate on monobromallylic alcohol:



Monobromallylic alcohol is obtained by the following series of reactions:—Allylic tribromide,  $C_3H_5Br_3$ , the product of the union of allylic bromide with bromine, is converted into dibromoglycid,  $C_3H_4Br_2$ , by the action of potassic hydrate; this compound on treatment with potassic acetate is readily converted into monobromallylic acetate,  $C_3H_4Br.C_2H_3O_2$ , which yields monobromallylic alcohol and potassic acetate on saponification by potassic hydrate.

Propargylic alcohol is a colourless mobile liquid, of



pleasant odour, specific gravity  $\cdot 9628$  at  $21^\circ$ ; boiling-point  $110^\circ$ – $115^\circ$ . It produces a white precipitate,  $C_3H_2Ag(OH)$ , in an ammoniacal solution of argentic nitrate, and a yellowish precipitate,  $(C_3H_2.OH)_2Cu_2$ , in an ammoniacal solution of cuprous chloride; it combines directly with bromine and hydrobromic acid.

Three tertiary alcohols of this series are known, viz. diallylmethylcarbinol, diallylpropylcarbinol and diallyliso-propylcarbinol. They are formed by the action of zinc on a mixture of allylic iodide and ethylic acetate, butyrate or isobutyrate. Camphol or borneol also belongs to the  $C_nH_{2n-3}.OH$  series.

$C_nH_{2n-7}.OH$  SERIES OF MONOHYDRIC ALCOHOLS.  
PHENOLS AND ALCOHOLS OF THE BENZYLIC SERIES.

These alcohols are the derivatives of the hydrocarbons of the  $C_nH_{2n-6}$  series. It has been pointed out already that these hydrocarbons act in the majority of cases as saturated compounds; the alcohols derived from them exhibit this behaviour, however, in a still more pronounced degree, in fact, they invariably give rise to the formation of substitution-derivatives, and never form additive compounds.

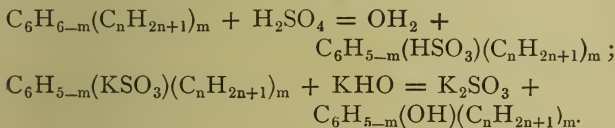
The most important and best investigated (first) member of the series is Phenol, which is the alcohol of benzene :



No isomerides of phenol are known, but three isomeric modifications of the next term, Cresol,  $C_7H_7.OH$ , exist, besides the metameric *benzylic alcohol*, which bears the same relation to the isomeric cresols that the monochlorinated compound formed by the action of chlorine on boiling toluene bears to the isomeric compounds obtained when the action of chlorine on toluene takes place in the cold or in presence of iodine. Hence two classes of alcohols are to be distinguished in this series :—1. The *phenols*, repre-

sented by the general formula,  $C_6H_{5-m}(OH)(C_nH_{2n+1})_m$ ; and 2. The alcohols of the *benzylic* series, represented by the general formula  $C_6H_{5-m} \left\{ \begin{matrix} C_nH_{2n}(OH)^1 \\ (C_nH_{2n+1})_m \end{matrix} \right.$ .

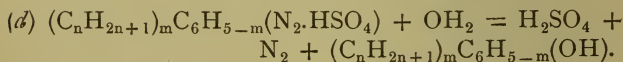
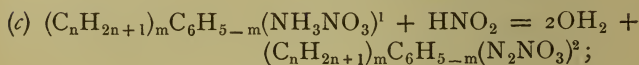
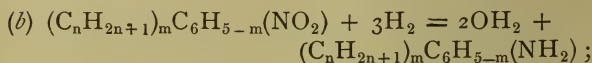
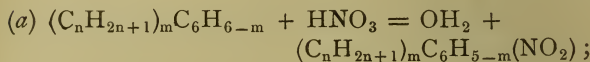
*General Methods of Formation.*—The phenols *cannot* be obtained from the corresponding mono-haloid substitution-derivatives of the  $C_nH_{2n-6}$  hydrocarbons, since potassic hydrate, argentic acetate, &c., are without action on these derivatives. The following are the two general methods usually employed in their preparation. 1. The hydrocarbon of the  $C_nH_{2n-6}$  series, corresponding to the phenol required, is converted by the action of concentrated sulphuric acid into the monosulphonic acid, and the potassic salt of this product is fused with potassic hydrate:



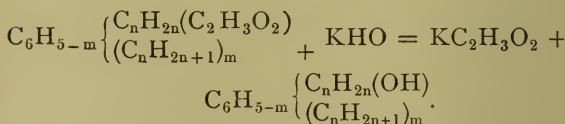
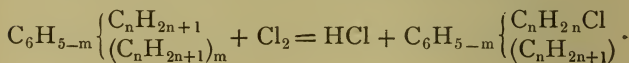
2. The hydrocarbon of the  $C_nH_{2n-6}$  series, corresponding to the phenol required, is converted into the mononitro-derivative by the action of nitric acid (*a*); this is reduced by nascent hydrogen to the amido-derivative (*b*), and an alco-

<sup>1</sup> These expressions are employed in order to include the formation of these alcohols from all the hydrocarbons of the benzene series. In the first term of the phenol series the value of *n* and *m* in the expression  $C_6H_{5-m}(OH)(C_nH_{2n+1})_m$  is zero; the highest possible value of *m* is doubtless 5; the limits within which *n* may vary cannot yet be determined, but it is to be borne in mind that in phenols derived from hydrocarbons formed by the introduction of several  $C_nH_{2n+1}$  groups in place of hydrogen in benzene, *n* may have the same or a different value in each of the groups, as in the case of *Xylenol* (*Dimethylphenol*),  $C_6H_3(CH_3)_2.OH$ , and *Thymol* (*Methylpropylphenol*),  $C_6H_3(OH) \left\{ \begin{matrix} CH_3 \\ C_3H_7 \end{matrix} \right.$ , the highest known term of the series, respectively. The same may be said of the alcohols of the benzylic series, in which, however, the lowest value of *n* in the  $C_nH_{2n}(OH)$  group is 1; *m* in the first term equals zero.

holic solution of a salt (usually the nitrate) of this derivative is then acted upon by nitrous acid (*c*) ; the diazo-salt produced is converted into the corresponding sulphate by treatment with sulphuric acid ; and finally this salt is decomposed by boiling with water (*d*) :



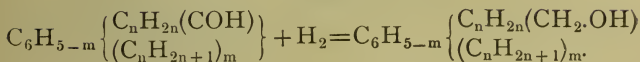
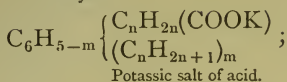
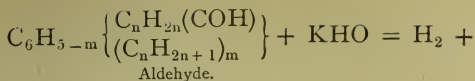
The alcohols of the benzylic series are obtained by the following methods :—1. By saponifying the acetates formed by the action of potassic acetate on the mono-haloid derivatives of the hydrocarbons of the benzene series, prepared by the action of chlorine on the boiling hydrocarbons :



2. By the action of an alcoholic solution of potassic hydrate on the corresponding aldehydes, together with the corresponding acid of the benzoic series :

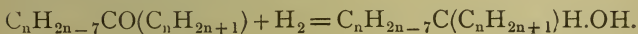
<sup>1</sup> Nitrate of amido-derivative.

<sup>2</sup> Nitrate of diazo-derivative.



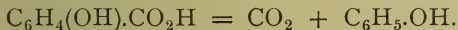
Primary alcohols alone are obtained by this method.

3. By the action of nascent hydrogen on the ketones of the form  $\text{C}_n\text{H}_{2n-7}\text{CO}(\text{C}_n\text{H}_{2n+1})$ :



By this method secondary alcohols are obtained.

PHENOL (*Oxybenzene*, *Carbolic Acid*),  $\text{C}_6\text{H}_5.\text{OH}$ , is obtained by the above general methods; also by distilling the three isomeric oxybenzoic acids, either alone or mixed with powdered glass, or caustic lime:



The chief source of phenol is coal-tar, from which it is prepared by submitting the coal-tar oil to distillation, and collecting apart the portion which distils over between  $150^\circ$  and  $200^\circ$ . This is mixed with a solution of sodic hydrate, the solution separated from the undissolved portion, decomposed by hydrochloric acid, and the oil thus obtained placed in contact with calcic chloride to render it anhydrous, and then purified by fractional distillation. It is then exposed to a low temperature, and the crystals which form are drained from the mother liquor, and again distilled.

Phenol crystallises at ordinary temperatures in long colourless needles, which melt at  $34^\circ$ – $35^\circ$  and boil at  $184^\circ$ . It is sparingly soluble in water, but dissolves readily in alcohol, ether, and acetic acid. It has a peculiar, not unpleasant odour, and acts as a powerful caustic when applied

to the skin. By far the most valuable property of phenol is that of preventing putrefaction, and of preserving animal substances from decomposition ; it even removes the fetid odour from meat and other substances already in a state of decomposition, hence it is largely employed as a disinfectant.

Phenol is scarcely altered by passing through a red-hot tube. It yields benzene when distilled over heated zinc-dust :  $\text{C}_6\text{H}_6\text{O} + \text{Zn} = \text{ZnO} + \text{C}_6\text{H}_6$ .

Phenol dissolves in sulphuric acid with evolution of heat and production of two isomeric monosulphonic acids of the formula  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{SO}_3\text{H}$  (phenolortho- and phenolpara-sulphonic acid), which are converted by the continued action of the acid into one and the same phenoldisulphonic acid,  $\text{C}_6\text{H}_3\cdot\text{OH}(\text{SO}_3\text{H})_2$ . On fusion of the potassic salts of these two isomeric phenolmonosulphonic acids with potassic hydrate, two isomeric dioxybenzenes are produced :



Chlorine acts readily upon phenol, and finally converts it into pentachlorophenol,  $\text{C}_6\text{Cl}_5\cdot\text{OH}$ . The first product is a mixture of two isomeric *monochlorophenols* ; the second is also a mixture of two *dichlorophenols* ; the third product appears to consist of a single *trichlorophenol*. Bromine exerts a precisely similar action. Iodophenols have been prepared by the action of iodine on phenol in presence of iodic acid or mercuric oxide. Three isomeric moniodophenols have thus been obtained, which are distinguished by the prefixes para-, meta-, and ortho- ; these exhibit different physical properties, and are especially characterised by their behaviour on fusion with potassic hydrate (p. 176).

Nitric acid acts violently upon phenol ; the first product is a mixture of two isomeric mononitrophenols, one of which is insoluble in water, extremely volatile in a current of steam, yellow in colour, has a peculiar aromatic odour, and melts at  $42^\circ$ , whilst the other is soluble in water, and crystallises in long white inodorous needles melting at  $112^\circ$ . The

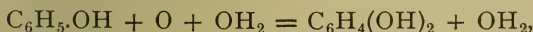
latter of these is converted into  $\alpha$ -dinitrophenol melting at  $114^\circ$  on further nitration ; the former, when similarly treated, also yields  $\alpha$ -dinitrophenol, but together with an isomeric ( $\beta$ ) dinitrophenol melting at  $69^\circ$ . The final product of the action of nitric acid on phenol is trinitrophenol,  $C_6H_2(NO_2)_3.OH$ , (*picric acid*), of which no isomeric modifications are known.

Phenol is converted by potassic hydrate into a metallic derivative  $C_6H_5.OK$ , but it does not decompose potassic carbonate. The above nitro-derivatives, however, have far more pronounced acid properties ; they readily decompose the metallic carbonates, and yield a series of crystalline yellow or red metallic derivatives, such as  $C_6H_4(NO_2).OK$ , &c.

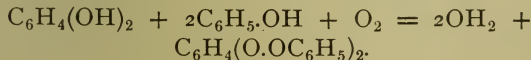
Trinitrophenol has the property of forming crystalline compounds with hydrocarbons such as benzene, naphthalene, anthracene, &c.

Phenol and its homologues are not attacked by the haloid acids, except perhaps when heated therewith under pressure at relatively very high temperatures ( $200^\circ$ – $300^\circ$ ). The haloid phosphorus compounds acting upon phenol and its homologues convert them into the corresponding mono-haloid derivatives of the  $C_nH_{2n-6}$  series of hydrocarbons.

Phenol exhibits a peculiar behaviour on oxidation with chromic acid, whereby it is converted into *phenoquinone*. Probably the first oxidation-product is *hydroquinone*:



the phenoquinone being the product of the simultaneous oxidation of this hydroquinone and phenol ; thus :



CRESOL (*Cresylic Acid*),  $C_7H_7.OH = C_6H_4(CH_3).OH$ .—The three known modifications are distinguished by the prefixes *para*-, *meta*-, and *ortho*-. Para- and orthocresol are respectively obtained by fusing the pure potassic salts of the two isomeric sulphonic acids produced on heating toluene with sulphuric acid with potassic hydrate. Paracresol is



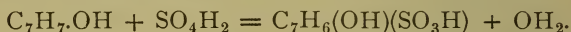
also obtained from crystalline nitrotoluene (p. 125) by the second general method of preparation. Metacresol has been produced by heating thymol,  $C_{10}H_{14}O$  (a crystalline phenol which exists in the volatile oils of thyme and horse-mint), with phosphoric anhydride, when propylene and cresol-phosphoric acid are produced; the latter yields metacresol and potassic phosphate on fusion with potassic hydrate. Coal-tar oil contains paracresol and (probably) orthocresol.

Paracresol is a solid crystalline body at ordinary temperatures, which boils at  $198^{\circ}$ – $200^{\circ}$ ; it yields potassic *paroxybenzoate*,  $C_6H_4(OH).CO_2K$ , on fusion with potassic hydrate.

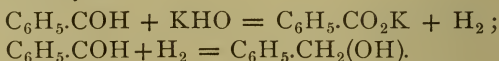
Metacresol is liquid and boils between  $195^{\circ}$ – $200^{\circ}$ ; oxidised by fusion with potassic hydrate, it yields potassic *metoxybenzoate*.

Orthocresol is also liquid, but boils at about  $189^{\circ}$ ; potassic *salicylate* (orthoxybenzoate), isomeric with potassic met- and par-oxybenzoates, is formed from it on oxidation by fusion with potassic hydrate.

Heated with sulphuric acid the three isomeric cresols yield three isomeric cresolsulphonic acids :



BENZYLIC ALCOHOL,  $C_6H_5.CH_2.(OH)$ , metameric with cresol, is produced simultaneously with potassic benzoate by the action of an alcoholic solution of potassic hydrate on benzoic aldehyde :



Also by saponification of benzylic acetate, prepared by heating benzylic chloride (p. 119) with potassic acetate. It is a colourless, strongly refracting, oily liquid, which boils at  $206^{\circ}$ . On treatment with nitric acid it is oxidised to benzoic aldehyde,  $C_6H_5COH$ . Hydrochloric acid converts it readily into benzylic chloride,  $C_6H_5.CH_2Cl$ . Concentrated sulphuric acid converts it into a resin-like substance.

It is thus evident that there is an enormous difference in

chemical behaviour between benzylic alcohol, which in all respects is a compound analogous to the alcohols of the ethylic series, and the corresponding phenol, cresol. A precisely similar relation obtains between the homologues of the phenols and of benzylic alcohol.

*Summary.*—The phenols differ, it will have been observed, from the alcohols of the preceding series in somewhat the same way that the hydrocarbons of the  $C_nH_{2n-6}$  series, excepting dipropargyl, differ from those of the isologous series richer in hydrogen. They are formed by special methods, behave as saturated compounds, are peculiarly stable, and yield well-characterised substitution-derivatives when acted upon by chlorine, nitric acid, &c., whereas the alcohols of the preceding (and benzylic) series do not yield such derivatives under similar conditions; the phenols behave differently on oxidation, they are not acted upon by the haloid acids, and, finally, they are especially characterised by yielding sulphonic acids when acted upon by sulphuric acid, which are convertible into dihydric alcohols (dioxy-derivatives of the  $C_nH_{2n-6}$  hydrocarbons) by fusion with potassic hydrate, whereas the isologous monohydric alcohols, proportionately richer in hydrogen, yield acid ethereal salts when similarly treated, which readily undergo reconversion into the alcohol and sulphuric acid, even when heated with water.

#### $C_nH_{2n-9}.OH$ SERIES OF MONOHYDRIC ALCOHOLS.

Only two alcohols of this series are known.

CINNAMIC OR PHENYLALLYLIC ALCOHOL,  $C_9H_9.OH = C(C_6H_5)H : CH.CH_2(OH)$ , is obtained by heating styracin,  $C_9H_7O_2.C_9H_9$  (a constituent of liquid storax and Peru balsam), with potassic hydrate solution. It crystallises in silky needles, which melt at  $33^\circ$ ; on oxidation it is converted into cinnamic aldehyde,  $C_9H_8O$ ; it forms with bromine a dibromide,  $C_9H_9Br_2.OH$ ; and by the action of nascent hydrogen it is in part converted into allylbenzene, in part converted into phenylpropylic alcohol,  $C(C_6H_5)H_2.CH_2.CH_2(OH)$ .

CHOLESTERIN,  $C_{26}H_{43}.OH$ , is a crystalline substance present in various parts of the animal system, in biliary calculi, and in the fat extracted from the fleece of sheep. On treatment with  $PCl_5$  it yields cholesterylic chloride,  $C_{26}H_{43}Cl$ ; by the action of cold fuming nitric acid it is converted into dinitrocholesterin,  $C_{26}H_{42}(NO_2)O$ .

$C_nH_{2n-13}.OH$  SERIES OF MONOHYDRIC ALCOHOLS.

$\alpha$ - and  $\beta$ -*naphthol*,  $C_{10}H_7.OH$ , two crystalline compounds which are in every respect analogues of the phenols, obtained by fusing the potassic salts of  $\alpha$ - and  $\beta$ -naphthalene-sulphonic acids with potassic hydrate, are the only known alcohols of the series.

$C_nH_{2n}(OH)_2$  SERIES OF DIHYDRIC ALCOHOLS. GLYCOLS.

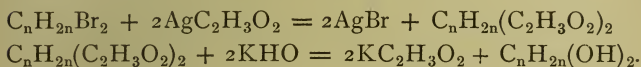
The glycols bear the same relation to the monohydric alcohols of the series  $C_nH_{2n+1}.OH$  that the dichlorinated paraffins bear to the monochlorinated paraffins; in other words, they may be regarded as the *di-hydroxyl* derivatives of the paraffins. The following have been obtained, but our knowledge of most of them is extremely imperfect:—

|                              |                   | Primary.<br>B.-P. | Isoprimary, Second-<br>ary, or Tertiary.<br>B.-P. |
|------------------------------|-------------------|-------------------|---------------------------------------------------|
| Ethylene glycol              | $C_2H_4(OH)_2$    | 197°·5            | —                                                 |
| Propylene „ (2 mods.)        | $C_3H_6(OH)_2$    | 208°–218°         | 188°–189°                                         |
| Tetrylene or butylene glycol | $C_4H_8(OH)_2$    | —                 | 183°–184°                                         |
| Pentylene or amylene glycol  | $C_5H_{10}(OH)_2$ | —                 | 177°                                              |
| Hexylene glycol              | $C_6H_{12}(OH)_2$ | —                 | 207°                                              |
| Octylene „                   | $C_8H_{16}(OH)_2$ | —                 | 235°–240°                                         |

Our experience of the chemical behaviour of these compounds is chiefly derived from the study of the first member of the series, to which the simple name of *glycol* is applied.

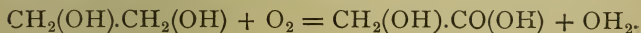
In most text-books attention is drawn to the fact that the difference between the boiling-points of the successive terms of this series appears to be in a contrary direction to that observed in other homologous series, i.e., that the lower members have higher boiling-points than the more complex terms of the series. At present slight weight attaches to this observation, however, since the known glycols are not strictly homologous; in other words, they do not all belong to the same isomeric series: some are primary, others are isoprimaries, secondary, perhaps tertiary glycols, and the comparison of their boiling-points is therefore nugatory.

*Preparation.*—The one general method consists in acting upon the di-haloid derivatives (usually the bromo-derivatives) of the paraffins with potassic or argentic acetate, the resulting acetate being then saponified with potassic hydrate:

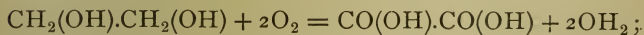


*Properties.*—The glycols are colourless, more or less viscid liquids, easily soluble in water and alcohol.

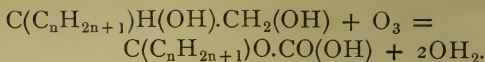
The oxidation of the glycols takes place at two stages: the first product is usually an oxyacid of the lactic series (general formula  $\text{C}_n\text{H}_{2n}(\text{OH}).\text{CO}_2\text{H}$ ); thus glycol yields *glycollic* acid (monoxyacetic acid):



The second product varies according to the nature of the glycol oxidised: in the case of the primary glycols, to which the general formula  $\text{CH}_2(\text{OH}).\text{C}_n\text{H}_{2n}.\text{CH}_2(\text{OH})$  may be assigned, a dibasic acid of the  $\text{C}_n\text{H}_{2n}(\text{CO}_2\text{H})_2$  series is always produced; thus glycol yields oxalic acid:

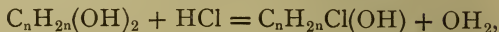


whereas the iso-glycols, represented by the general formula  $\text{C}(\text{C}_n\text{H}_{2n+1})\text{H}(\text{OH}).\text{CH}_2(\text{OH})$ , yield so-called *ketonic* acids as final oxidation-products, e.g.:



Little is known of glycols of other isomeric series.

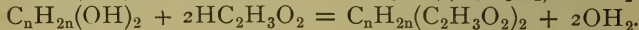
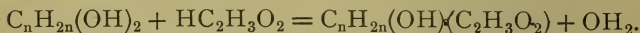
The glycols are readily acted upon by the haloid acids, in the first place according to the equation :



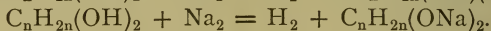
and by the continued action of these acids, or more readily under the influence of the haloid phosphorus compounds, they are converted into di-haloid derivatives of the corresponding paraffins :



By heating the glycols with acetic acid or its homologues in closed vessels, ethereal salts of these acids (compound ethers) are produced, e.g. :



Potassium and sodium act upon the glycols with evolution of hydrogen and formation of metallic derivatives :



*Polyethylenic glycols* are formed from glycol by progressive condensation with elimination of the elements of water.

The following are known :—

|                    |                                                                                             |
|--------------------|---------------------------------------------------------------------------------------------|
| Diethylenic glycol | $\text{C}_4\text{H}_{10}\text{O}_3 = 2\text{C}_2\text{H}_4(\text{OH})_2 - \text{OH}_2$      |
| Triethylenic „     | $\text{C}_6\text{H}_{14}\text{O}_4 = 3\text{C}_2\text{H}_4(\text{OH})_2 - 2\text{OH}_2$     |
| Tetrethylenic „    | $\text{C}_8\text{H}_{18}\text{O}_5 = 4\text{C}_2\text{H}_4(\text{OH})_2 - 3\text{OH}_2$     |
| Pentethylenic „    | $\text{C}_{10}\text{H}_{22}\text{O}_6 = 5\text{C}_2\text{H}_4(\text{OH})_2 - 4\text{OH}_2$  |
| Hexethylenic „     | $\text{C}_{12}\text{H}_{26}\text{O}_7 = 6\text{C}_2\text{H}_4(\text{OH})_2 - 5\text{OH}_2.$ |

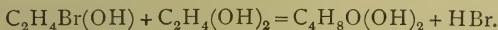
There is a difference in boiling-point of about 45° between each of these ; they are viscid liquids, becoming continually more viscid as they increase in complexity, and as the boiling-point rises.

One of the best general methods of preparation consists in heating glycol with ethylenic dibromide in closed tubes, for some hours, at  $110^{\circ}$ – $120^{\circ}$ . The nature of the product then depends on the proportions employed of these two bodies, and on the length of time during which they are heated together.

The first reaction which occurs probably consists in the formation of ethylenic-bromohydrate, thus :



which reacts upon the glycol (employed in excess) to form diethylenic glycol and hydrobromic acid :



By the action of this hydrobromic acid upon a further quantity of glycol, water and ethylenic bromohydrate are produced, and the latter reacting upon the diethylenic glycol converts it into triethylenic glycol and hydrobromic acid :

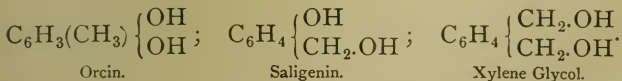


and by a similar cycle of operations, tetrethylenic glycol is produced from triethylenic glycol, &c.

$\text{C}_n\text{H}_{2n-8}(\text{OH})_2$  SERIES OF DIHYDRIC ALCOHOLS—ORCINS, AROMATIC GLYCOLS, AND ALCOHOLS OF THE SALIGENIN SERIES.

These are derived from the hydrocarbons of the  $\text{C}_n\text{H}_{2n-6}$  series, by methods in principle the same as those which give rise to the monohydric alcohols of the  $\text{C}_n\text{H}_{2n-7}(\text{OH})$  series.

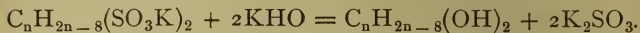
The series includes three classes of metameric compounds : the *orcins*, the *aromatic glycols*, and the *alcohols of the saligenin series*. The manner in which the members of these three classes are related will be evident on inspection of the following formulæ :



*Preparation of the Orcins.*—1. By fusion of the potassic salts

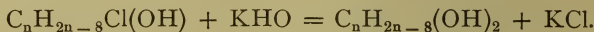


of the disulphonic acids obtained by the action of sulphuric acid on the hydrocarbons of the  $C_nH_{2n-6}$  series with potassic hydrate :



2. Similarly from the monosulphonic acids derived from the phenols.

3. By fusion of the mono-haloid derivatives of the phenols with potassic hydrate, e.g. :



The first term of the series of the composition  $C_6H_4(OH)_2$  includes three isomerides, *Resorcin*, *Pyrocatechin*, and *Hydroquinone*.

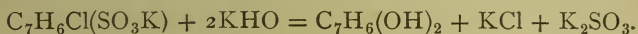
RESORCIN is obtained by the action of potassic hydrate on benzenedisulphonic acid,  $C_6H_4(SO_3H)_2$ ; on phenolparasulphonic acid,  $C_6H_4(OH)(SO_3H)$ ; and on paraiodophenol,  $C_6H_4I(OH)$ ; but is best prepared by fusing galbanum resin with potassic hydrate. It crystallises from water in tabular crystals, or prisms, which melt at  $99^\circ$ . It forms a dark violet-coloured liquid with ferric chloride, and reduces an ammoniacal solution of argentic nitrate at the boiling-heat.

PYROCATECHIN is obtained by the action of potassic hydrate on phenolmetasulphonic acid, or on metaiodophenol, and by the dry distillation of catechin and a number of other allied vegetable substances. It crystallises from water in laminæ which melt at  $116^\circ$ ; it yields a dark green colouration with solutions of ferric salts, and is further distinguished from resorcin by forming a white precipitate on the addition of plumbic acetate to its aqueous solution.

HYDROQUINONE is a product of the dry distillation of quinic acid, and is also obtained by fusion of orthiodophenol with potassic hydrate. It crystallises in rhombic crystals, and melts at  $177^\circ$ . It is readily distinguished from resorcin

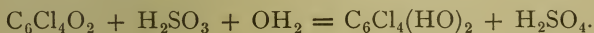
and pyrocatechin by its conversion into quinone on oxidation :  $C_6H_4(OH)_2 + O = C_6H_4O_2 + OH_2$ . Quinone is readily reconverted into hydroquinone by the action of nascent hydrogen.

ORCIN,  $C_6H_3(CH_3)(OH)_2$ , appears to exist ready formed in all the lichens used for the preparation of archil, cudbear, and litmus. It has been prepared synthetically by fusing the potassic salt of the sulphonic acid obtained by the action of sulphuric acid on monochlorotoluene with potassic hydrate

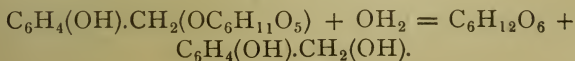


It crystallises from water in colourless six-sided prisms which melt at  $86^\circ$ . By the combined action of oxygen and ammonia it is converted into orcein,  $C_7H_7NO_3$ , an uncrySTALLISABLE substance, which dissolves in alcohol, forming a deep scarlet solution, and in aqueous alkalies with violet-red colour. Orcein is present among other colouring matters in commercial archil. A number of isomerides of orcin have been prepared, but little is known of them.

Both resorcin and orcin yield well-characterised haloid and nitro-derivatives when acted upon by the halogens and nitric acid. Haloid derivatives of pyrocatechin are not known. Haloid derivatives of hydroquinone are formed by the action of nascent hydrogen on the corresponding derivatives of quinone, thus tetrachloroquinone is converted by the action of aqueous sulphurous acid into tetrachlorhydroquinone :



SALICYLIC ALCOHOL (*Saligenin*) is obtained from salicin, a crystalline substance contained in the leaves of poplar, willow, and several other trees. On heating with diluted sulphuric acid, or on digestion with synaptase, or saliva, salicin is resolved into saligenin and glucose.



Saligenin crystallises in colourless nacreous scales ; it melts at  $82^{\circ}$  ; on oxidation it is converted into salicylic aldehyde,  $C_6H_4(OH).COH$ .

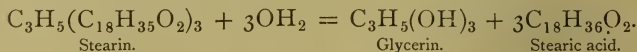
XYLENE GLYCOL,  $C_6H_4(CH_2.OH)_2$ , is prepared by digesting the dichlorinated derivative of paraxylene, obtained by the action of chlorine on the boiling xylene, with water at  $170^{\circ}$ . It forms crystalline needles which melt at  $112^{\circ}$  ; on oxidation it is converted into terephthalic acid,  $C_6H_4(CO.OH)_2$ .

### $C_nH_{2n-1}(OH)_3$ SERIES OF TRIHYDRIC ALCOHOLS.

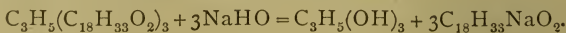
These may be regarded as the trihydroxyl substitution-derivatives of the paraffins. Two members of the series are known, viz. :

|             |   |   |   |   |   |                |
|-------------|---|---|---|---|---|----------------|
| Glycerin    | . | . | . | . | . | $C_3H_5(OH)_3$ |
| Amylgycerin | . | . | . | . | . | $C_4H_7(OH)_3$ |

GLYCERIN,  $C_3H_5(OH)_3 = C(CH_2.OH)_2H.OH$ .—Most animal and vegetable fats and fixed oils<sup>1</sup> are mixtures of ethereal salts formed from glycerin and acids of the acetic and oleic series. Thus mutton and beef fat consists mainly of *stearin* or stearic glyceride ; palm oil is chiefly palmitic glyceride (*palmitin*) ; olive oil is an oleic glyceride (*olein*). These glycerides are decomposed by heating with water, yielding glycerin and an acid, thus :



Glycerin is largely obtained as a by-product in the manufacture of *soap*, from the fats and fixed oils : the oil or fat is heated with an alkaline solution, whereby glycerin and an alkaline salt, or soap, as it is termed, are produced, thus :<sup>2</sup>

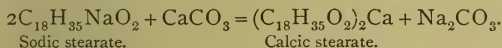


<sup>1</sup> These oils (palm oil, olive oil, &c.) are termed fixed, because they cannot be distilled without undergoing decomposition, in contradistinction to the turpentine oils, which volatilise unchanged.

<sup>2</sup> The decomposition of ethereal salts by caustic alkalies, whereby an alcohol and a metallic salt are formed, is commonly designated by the general term 'saponification.'

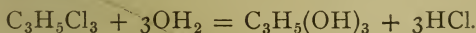
The soap is separated from the solution by the addition of common salt and the solution of sodic chloride (in which the soaps are insoluble) and glycerin is drawn off ; this spent-lye, as it is termed, is then submitted to distillation in a current of superheated steam. The glycerin passes over with a certain proportion of water, the greater part of which may be removed from it by evaporation, and the whole may be driven off by heating in vacuo to a temperature below the boiling-point of glycerin.

Ordinary hard soap is a mixture of sodic stearate, palmitate, and oleate; soft soap consists of the corresponding potassic salts; lead plaster is a plumbic oleate obtained by heating olive oil with plumbic oxide. Lime soap is obtained by saponifying the fats with slaked lime; lime soaps are insoluble in water, and the heavy curd formed on adding soap solution to *hard water* is a precipitate of lime soap formed by double decomposition from the calcic salts dissolved in the water and the soda soap:



Glycerin is now prepared on the large scale by the decomposition of the fats and oils by distillation in an atmosphere of superheated steam. The fats or oils are placed in a still, heated to a temperature between  $290^{\circ}$ – $310^{\circ}$ , and superheated steam passed up through them; the glycerin then distils over with the steam, and the acids remain in the still.

The synthesis of glycerin has been effected by digesting trichlorhydrin, one of the several isomeric trichloropropanes formed on heating propylene chloride (dichloropropane) with iodine chloride, with water in closed tubes at  $170^{\circ}$ :

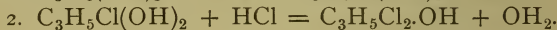
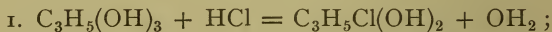


*Properties.*—Glycerin cannot be distilled under the ordinary atmospheric pressure without undergoing decomposition, but passes over undecomposed under a pressure of 50 mm. of mercury at about  $210^{\circ}$ , it also distils without decomposition in an atmosphere of steam. It is a syrupy, colour-

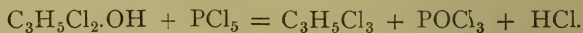
less, inodorous liquid, sweet to the taste, and neutral to test-paper, which is soluble in water in all proportions.

*Reactions.*—1. Glycerin is converted by careful oxidation by nitric acid into *glyceric acid*, but at the same time much oxalic acid is produced :  $C_3H_8O_3 + O_2 = C_3H_6O_4 + OH_2$ . Glyceric acid cannot be further oxidised without undergoing decomposition into acids containing fewer units of carbon, the chief among which is oxalic acid,  $H_2C_2O_4$ .

2. Glycerin is converted by the action of hydrochloric or hydrobromic acid, or of the corresponding haloid phosphorus compounds, into so-called *chlor-* or *bromhydrins*. The action of the haloid acids takes place by two stages : at the first, *monochlor-* or *monobromhydrin*, at the second, *dichlor-* or *dibromhydrin*, is produced :



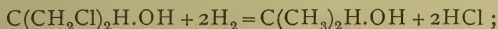
Phosphorus pentachloride and bromide have the same action, but also give rise to the formation of a third product, *trichlor-* or *tribromhydrin* :



The second product of the action of hydrochloric acid on glycerin is a mixture of two isomeric dichlorhydrins, which boil respectively at  $174^\circ$  and  $182^\circ$ . The latter of these is identical with the product of the action of chlorine on allylic alcohol. Trichlorhydrin and tribromhydrin are respectively identical with allylic trichloride and tribromide ; the former is among the products of the action of iodine chloride on propylene chloride. The chlor- and bromhydrins lose the elements of hydrochloric or hydrobromic acid when submitted to the action of potassic or sodic hydrate ; thus monochlorhydrin,  $C_3H_5Cl(OH)_2$ , is converted into Glycide,  $C_3H_5O.OH$  ; and dichlorhydrin,  $C_3H_5Cl_2.OH$ , yields epichlorhydrin,  $C_3H_5ClO$ . Epichlorhydrin behaves as an unsaturated compound, and combines with water to form monochlorhydrin, when heated with it under pressure ; it unites with hydrochloric acid to form the dichlorhydrin boiling at  $174^\circ$ , and since

both the above-mentioned dichlorhydrins yield the same epichlorhydrin on treatment with potassic hydrate, pure dichlorhydrin (B.P. 174°) may be obtained from glycerin by converting the mixture of dichlorhydrins into epichlorhydrin, and acting upon this with hydrochloric acid.

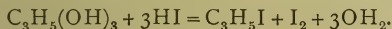
Monochlorhydrin is converted by the action of nascent hydrogen into propylene glycol,  $C_3H_6(OH)_2$ ; dichlorhydrin from epichlorhydrin similarly treated yields isopropylic alcohol :



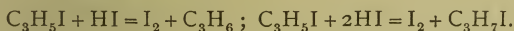
whilst the isomeride from allylic alcohol yields propylic alcohol.

3. Hydriodic acid and phosphorus iodide convert glycerin into allylic iodide, besides which propylene and isopropylic iodide are also obtained.

The formation of allylic iodide is represented by the equation:



At the same time, by the action of the hydriodic acid on the primary product, allylic iodide, the above-mentioned secondary products are formed, thus :



The primary product of the action of phosphorus iodide is also allylic iodide :  $2C_3H_5(OH)_3 + P_2I_4 = 2C_3H_5I + 2H_3PO_3 + I_2$ ; more or less hydriodic acid, however, is also produced, which reacts on the allylic iodide, as above explained.

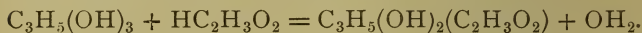
It is said that, under certain conditions, the action of hydriodic acid on glycerin forms a complex product of the formula :  $C_6H_{11}IO_3 = 2C_3H_8O_3 - 3OH_2 + HI$ , and it is suggested that this product is possibly identical with a compound containing iodine, present in cod-liver oil.

4. When heated alone or with dehydrating agents, glycerin is decomposed with formation of *acrolein*,  $C_3H_4O$ , recognised by its intensely irritating acrid odour, and other products :  $C_3H_8O_3 = 2OH_2 + C_3H_4O$ .

5. By heating glycerin with the organic acids in closed

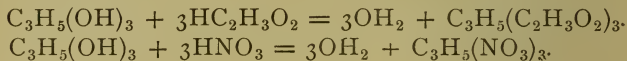


vessels, so-called *glycerides* or glyceric ethers are produced. The proportions in which the acid and glycerin enter into reaction vary according to the proportions in which they are mixed, the temperature to which the mixture is subjected, and the time during which the heating is continued. Thus acetic acid and glycerin yield *monacetin*,  $\text{C}_3\text{H}_5(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)$ ; *diacetin*,  $\text{C}_3\text{H}_5(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_2$ ; and *triacetin*,  $\text{C}_3\text{H}_5(\text{C}_2\text{H}_3\text{O}_2)_3$ ; which are formed in the manner indicated by the equation:—



In this way Berthelot has succeeded in preparing *Tristearin*, *Tripalmitin*, and *Triolein*, from stearic, palmitic, and oleic acids and glycerin, the bodies thus obtained being found identical in all respects with stearin, palmitin, and olein from natural fats.

6. Glyceric ethereal salts are also obtained by the action of the mineral oxyacids on glycerin. Thus glycerin is converted into the so-called *nitroglycerin* by adding it to a carefully cooled mixture of nitric and sulphuric acids. The formation of this compound from glycerin and nitric acid is analogous to that of triacetin from glycerin and acetic acid:



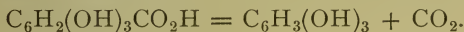
Nitroglycerin, or *glycerotrinitrin*, as it is more correctly termed, is a light yellow, violently explosive, oily liquid, of sp. gr. 1.6 at 15°. By the action of potassic hydrate, it is converted into glycerin and potassic nitrate, just as triacetin is converted into glycerin and potassic acetate.

7. Glycerin cannot be fermented by pure yeast, but it readily undergoes fermentation in contact with *Bacillus subtilis*, yielding ethylic alcohol as principal product; by means of another *Bacillus*, however, it may be fermented to normal butylic alcohol and butyric acid (Fitz).

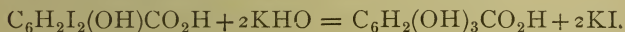
$C_nH_{2n-9}(OH)_3$  SERIES OF TRIHYDRIC ALCOHOLS.

The only known members of this series are the so-called pyrogallic acid, or pyrogallol, as it is more appropriately termed,  $C_6H_3(OH)_3$ , and its isomeride phloroglucin.

Pyrogallol is obtained by dry distillation of gallic acid :



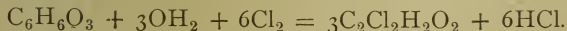
The relation of pyrogallol to benzene is evident from the fact that it yields that hydrocarbon when distilled at a red heat over zinc-dust, and that gallic acid is obtained by fusing diiodosalicylic acid with potassic hydrate :



Pyrogallol crystallises in long white flattened prisms ; it melts at  $115^\circ$ . The aqueous solution slowly absorbs oxygen on exposure to the air, becoming brown ; this change occurs very rapidly in presence of alkalies, hence a solution of pyrogallol and potassic hydrate is employed as an absorbent of oxygen in gas analysis. By the action of acetic chloride it is converted into triacetypyrogallol,  $C_6H_3(C_2H_3O_2)_3$  ; on treatment with bromine it yields tribromopyrogallol,  $C_6Br_3(OH)_3$ .

Phloroglucin is obtained on fusion of phloretin, catechin, kino, dragon's blood, quercitin, and a number of similar substances with potassic hydrate. Phloroglucin crystallises in large colourless prisms of the composition  $C_6H_6O_3 \cdot 2OH_2$  ; in the anhydrous condition it melts at  $220^\circ$ . Triaceto-phloroglucin,  $C_6H_3(C_2H_3O_2)_3$ , is obtained from it on treatment with acetic chloride, and tribromophloroglucin on treatment with bromine.

By the action of chlorine on an aqueous solution of phloroglucin, dichloroacetic acid is produced :



Phloroglucin may be obtained by fusing phenol with sodic hydrate, which proves that it is a trihydroxy-derivative of benzene.

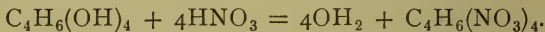
$C_nH_{2n-2}(OH)_4$  SERIES OF TETRAHYDRIC ALCOHOLS

The only alcohol of this series at present known is *Erythrite* (*erythromannite*, *phycite*),  $C_4H_6(OH)_4$ , a saccharine substance which exists ready formed in *Protococcus vulgaris*, and which may also be obtained from any of the varieties of *Rocella tinctoria* by boiling with excess of lime or baryta.

It forms large colourless transparent crystals, easily soluble in water. It is converted into a moniodo-derivative of the paraffin tetrane by distillation with hydriodic acid :



The iodotetrane thus obtained is convertible into secondary butylic alcohol (p. 158). Nitric acid converts erythrite into *erythrotetranitrin* (so-called nitroerythrite) :

 $C_nH_{2n-4}(OH)_6$  SERIES OF HEXHYDRIC ALCOHOLS.

*Mannite* and *Dulcite*, two of the natural sugars, are members of this series.

MANNITE,  $C_6H_8(OH)_6$ , is the chief component of *Manna*, the dried sap of *Fraxinus ornus*, from which it may be extracted by boiling alcohol. It is also present in the sap of the apple, cherry, larch, and lime, in many seaweeds, and in mushrooms. It may be produced by the action of nascent hydrogen (sodium amalgam) on an aqueous solution of cane sugar<sup>1</sup> inverted by boiling with a small quantity of sulphuric acid :  $C_6H_{12}O_6 + H_2 = C_6H_{14}O_6$ .

Mannite crystallises in colourless four-sided prisms, or fine needles, easily soluble in water and alcohol, insoluble in ether ; it is slightly sweet ; mannite does not ferment in contact with yeast, nor does it reduce an alkaline solution

<sup>1</sup> Such a solution contains a mixture of dextrose and lævulose, both of which apparently yield mannite.

of cupric hydrate on boiling (distinction from the glucoses) ; it has no action on polarised light.

Hydriodic acid converts mannite into an iodohexane ( $\beta$ -hexylic iodide), from which normal secondary hexylic alcohol may be obtained :



It yields various ethereal salts when heated with acids such as acetic acid, &c. ; concentrated nitric acid, for example, converts it into so-called *nitromannite* (mannitohexanitrin),  $\text{C}_6\text{H}_8(\text{NO}_3)_6$ , a crystalline substance which detonates violently by percussion, and is reconverted into mannite by the action of reducing agents. Mannite also forms metallic derivatives : thus a crystalline precipitate of the composition  $\text{C}_6\text{H}_{10}\text{Pb}_2\text{O}_6$  is produced on adding mannite to an ammoniacal solution of plumbic acetate.

Mannite yields two characteristic oxidation-products : *mannitic acid*,  $\text{C}_6\text{H}_{12}\text{O}_7$ , obtained by moistening platinum black with mannite solution;<sup>1</sup> and *saccharic acid*,  $\text{C}_6\text{H}_{10}\text{O}_8$ , the product of the action of dilute nitric acid.

**DULCITE** (*dulcin*, *dulcose*, *melampyrite*),  $\text{C}_6\text{H}_8(\text{OH})_6$ , the isomeride of mannite, has been produced artificially by the action of nascent hydrogen on inverted milk-sugar (see lactose). Dulcite was first obtained from a substance of unknown origin, imported from Madagascar ; it may be extracted from the expressed juice of *Melampyrum nemorosum* and other *Melampyrum* species.

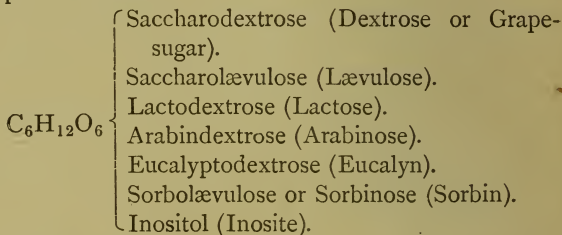
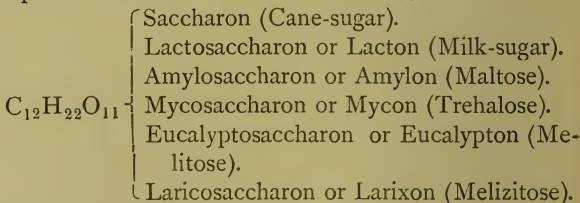
Dulcite closely resembles mannite in properties, but crystallises in monoclinic prisms (mannite in triclinic prisms) and melts at  $182^\circ$  (mannite at  $165^\circ$ ). When oxidised by nitric acid, it is converted into *mucic acid*, isomeric with saccharic acid. It yields the same iodohexane as mannite when heated with hydriodic acid, and is converted by concentrated nitric acid into *dulcithexanitrin* :  $\text{C}_6\text{H}_8(\text{NO}_3)_6$ .

<sup>1</sup> *Mannitose*,  $\text{C}_6\text{H}_{12}\text{O}_6$ , an isomeride of glucose, is obtained simultaneously with mannitic acid.

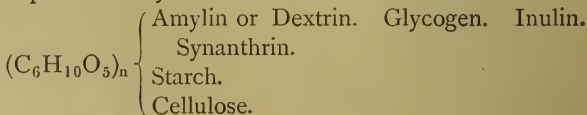
## CARBOHYDRATES.

This name is applied to a variety of substances like cane-sugar, starch and cellulose, the composition of which is represented by the general formula  $C_n(OH_2)_m$ : i.e. they are compounds of carbon with oxygen and hydrogen, the two latter elements being present in the proportions in which they form water. The majority occur naturally either in animals or plants, and many of them are of the highest physiological importance. They may conveniently be arranged in three groups, according to their empirical composition, thus :

## Group I. Glucoses.

Group II. Saccharons.<sup>1</sup>

## Group III. Amyloids.



<sup>1</sup> It appears highly desirable to distinguish the members of the two great groups of carbohydrates of the formula  $C_6H_{12}O_6$  and  $C_{12}H_{22}O_{11}$  by names having distinct terminals, and to restrict the terminal *ose* to the former.

Most of the carbohydrates are capable when in solution of rotating, as it is termed, rays of plane polarised light, and are therefore said to be optically active. Thus, if monochromatic yellow light, such as is furnished by a Bunsen gas flame in which a sodium salt is volatilised, be passed through a Nicol's prism, and a second similar prism be placed at some little distance in front of the first, it will be found that when the prisms are arranged with their 'principal sections' at right angles no light will pass through the second prism; but on interposing between them a glass cell with parallel sides, or a tube closed at the ends with parallel plates of glass, filled with a strong solution of cane-sugar, the field of view will become illuminated, and in order to darken it again the second prism must be turned through a certain angle in the direction in which the hands of a watch move. Such a solution is said to be dextrorotatory. A given substance always exhibits the same rotatory power under the same set of conditions, but different substances exhibit different *specific rotatory powers*, and this property therefore affords a most valuable means of distinguishing the various carbohydrates.

The specific rotatory power  $[\alpha]$  of a substance for light of any particular refrangibility is the angular deviation imparted to the ray observed by a column of unit length,  $l$ , and density,  $d$ , and is expressed by the formula

$$1. \quad [\alpha] = \frac{\alpha}{l \cdot d}.$$

It is usual to take the decimeter as the unit of length. If the observation be made for light of the refrangibility of the D lines of the solar spectrum, the symbol  $[\alpha]_D$  stands for the specific rotatory power; if for light of the refrangibility of the mean yellow portion of the spectrum, it is indicated by the symbol  $[\alpha]_j$ .

This formula, however, applies only to bodies which can be examined *per se*; and if a solution of an optically active substance in an inactive solvent be employed for the determination, the specific rotatory power is deduced with the aid of the formula

$$2. \quad [\alpha] = \frac{\alpha}{l \cdot e \cdot d},$$

where  $e$  is the amount of active substance in a unit of weight of solution, and  $d$  the density of the solution. If, as is frequently



done, the amount of active substance in 100 parts by weight of the solution be determined, indicating this by  $p$ , the formula becomes

$$3. \quad [\alpha] = \frac{100 \ a}{l \cdot p \cdot d}.$$

Or, if merely the concentration  $c$ , i.e. the number of grams of active substance in 100 c.c. of solution, be ascertained, since  $c = dp$ , we have

$$4. \quad [\alpha] = \frac{100 \ a}{l \cdot c}.$$

It has been found, however, that the rotatory power of a substance is always more or less modified by association with an optically inactive solvent; hence the specific rotatory power of a substance deduced by formula 2, 3 or 4 is merely the *apparent* and not the *absolute* specific rotatory power, *and the value obtained is applicable only to the solution of the particular strength and character used*. A description of the instruments for determining specific rotatory power will be found in Watts' 'Dictionary of Chemistry,' vol. viii., pt. ii., art. Light.

Several carbohydrates exhibit the phenomenon of *birotation*, i.e. the apparent specific rotatory power in a solution freshly prepared without heating is different from the apparent specific rotatory power in a solution which has been prepared some time or which has been heated. Thus, the initial rotatory power of dextrose is about double the constant rotatory power. Milk-sugar in like manner has an initial rotatory power about one and a half times its constant rotatory power. The initial rotatory power of amylo-*n*, however, is somewhat lower than its constant rotatory power.

Another property of importance possessed by many carbohydrates is that of reducing an alkaline solution of a cupric salt. When proper precautions are observed, and provided that the conditions are constant, the same carbohydrate always exercises the same *cupric reducing power*, but there are considerable differences between the various carbohydrates, as shown by the following table, in which the cupric reducing powers of equal weights of a number of them in 1 per cent. solutions are contrasted with that of dextrose taken as 100 (Soxhlet):

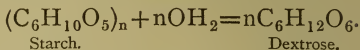
|                                                     |      |
|-----------------------------------------------------|------|
| Dextrose . . . . .                                  | 100  |
| Invert-sugar (mixture of dextrose and lævulose) .   | 96·2 |
| Lævulose (?) . . . . .                              | 92·4 |
| Milk-sugar . . . . .                                | 70·3 |
| Lactose . . . . .                                   | 93·2 |
| Milk-sugar after heating with dilute sulphuric acid | 96·2 |
| Maltose . . . . .                                   | 61·0 |

The cupric solution used is known as Fehling's solution, and is prepared by mixing solutions of cupric sulphate, potassic sodic tartrate and sodic hydrate, so that 1 litre of solution contains 34·639 grams  $\text{CuSO}_4$ , 173 grams  $\text{NaKC}_4\text{H}_4\text{O}_6$  and 52 grams  $\text{NaOH}$ ; the addition of the tartrate prevents the precipitation of cupric hydrate by the sodic hydrate. On warming such a solution with a solution of dextrose, cuprous oxide is precipitated: the blue colour disappearing entirely if sufficient carbohydrate be present. 5 gram of dextrose in a 1 per cent. solution reduces 105·2 cubic centimetres of Fehling's solution, but if the latter be diluted with 4 volumes of water the dextrose exerts a slightly diminished rotatory power in the proportion of 10·52 : 10·11; if an excess of the Fehling's solution be used, a somewhat larger amount of reduction is effected. It would appear, in fact, that the initial products of oxidation of the carbohydrate are themselves more or less acted upon, so that the observed value does not accurately represent the cupric reducing power of the carbohydrate alone.

#### GROUP I. GLUCOSES : $\text{C}_6\text{H}_{12}\text{O}_6$ .

DEXTROSE (*Dextro-glucose, Ordinary Glucose or Grape-sugar*),  $\text{C}_6\text{H}_{12}\text{O}_6$ .—This carbohydrate is widely distributed throughout the vegetable kingdom; it is present in the juice of ripe grapes and in fact of all ripe fruits, and it constitutes the solid crystalline portion of honey: but in these cases it always occurs together with lævulose, and usually also with cane-sugar, which is capable of yielding both dextrose and lævulose. It is present in considerable quantity (even to the extent of ten per cent.) in diabetic urine, and is found in small quantities in nearly all animal fluids, such as blood, chyle, in the liver, and in normal healthy urine, but un-

accompanied by lævulose. It is the ultimate product of the *hydrolysis*<sup>1</sup> of starch by dilute sulphuric acid :



Cellulose is also converted into dextrose by prolonged digestion with sulphuric acid. It is a product of the action of *hydrolytic agents* on many glucosides<sup>2</sup>; and some of the albuminoid substances and brain matters also furnish dextrose on hydrolysis. It is best prepared from cane-sugar, and purified by crystallisation from methylic alcohol (Soxhlet).

Dextrose is excessively soluble in water, and crystallises from a concentrated solution in cauliflower-like masses of the composition  $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ ; from methylic alcohol it crystallises in glistening anhydrous prisms. It is less sweet than cane-sugar. Its solution turns a ray of polarised light to the right, hence the name dextroglucose and dextrose; in an 18.5 per cent. solution it has the *apparent* specific rotatory power  $[\alpha]_D = 52^\circ.85$  (Soxhlet), its *absolute* specific rotatory power, according to Tollens, being  $[\alpha]_D = 58^\circ.70$ .

Dextrose unites with sodic chloride, forming a crystalline compound of the formula  $(\text{C}_6\text{H}_{12}\text{O}_6)_2 \cdot \text{NaCl} \cdot \text{OH}_2$ . Highly

<sup>1</sup> Decompositions like that of starch into dextrose, of cane-sugar into dextrose and lævulose, of the fats into glycerin and an acid, or of ordinary ether into ethylic alcohol, which involve the fixation of the elements of water, may all be said to be the result of *hydrolysis*; and those substances which, like sulphuric acid, diastase, emulsin, &c. induce hydrolysis may be termed hydrolytic agents or *hydrolysts*. The substance hydrolysed is the *hydrolyte*. The mere fixation of the elements of water unaccompanied by decomposition, as in the conversion of ethylenic oxide into glycol,  $\text{C}_2\text{H}_4\text{O} + \text{OH}_2 = \text{C}_2\text{H}_4(\text{OH})_2$ , may be termed *hydration* in contradistinction.

<sup>2</sup> The glucosides are a class of natural products, of frequent occurrence in plants, which on hydrolysis always furnish a glucose and some other substance or substances; salicin, for example, a constituent of willow bark, yields saligenin and glucose (p. 177), and amygdalin from bitter almonds—which, however, is perhaps a *saccharide*, i.e. a derivative of a saccharon and not of a glucose—yields benzaldehyde, hydrocyanic acid and glucose (p. 234).

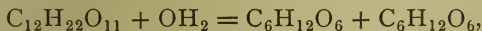
unstable metallic derivatives may be obtained by dissolving lime, baryta, or oxide of lead in an aqueous solution of dextrose and precipitating by alcohol; the baric derivative has the composition  $(C_6H_{11}O_6)_2Ba$ .

If dextrose be heated with a mixture of acetic anhydride and fused sodic acetate on the water bath, an octaceto-derivative of the composition  $C_{12}H_{14}O_3(C_2H_3O_2)_8$  is obtained, which is isomeric with the compound got by heating cane-sugar with acetic anhydride. This acetate yields sodic acetate and a carbohydrate isomeric with cane-sugar on treatment with sodic hydrate.

Dextrose is slowly altered, even in the cold, by aqueous solutions of the alkalies or alkaline earths, and rapidly on heating, the liquid becoming first yellow and afterwards brown; one of the products of the action of calcic hydrate is an isomeride of cane-sugar (Peligot). It is readily oxidised, and therefore quickly reduces alkaline solutions of silver and copper salts, causing the precipitation of metallic silver or cuprous oxide; its cupric reducing power is approximately represented by the proportion  $C_6H_{12}O_6 : 5CuSO_4$ . On boiling it with dilute sulphuric or hydrochloric acid, brown humus-like substances are formed. Dilute nitric acid oxidises dextrose to saccharic acid,  $C_4H_4(OH)_4(COOH)_2$ .

A dilute solution of dextrose mixed with yeast rapidly undergoes fermentation at a temperature of  $20^{\circ}$ – $25^{\circ}$ .

LÆVULOSE,  $C_6H_{12}O_6$ , occurs, as already mentioned, together with dextrose in the juice of ripe fruits, honey, &c. It is obtained, together with an equal quantity of dextrose, on heating a solution of cane-sugar with dilute acids:



and may be separated from it by mixing the solution of *invert-sugar*, as the product is termed, with slaked lime. A solid calcium-derivative of lævulose is formed which is separated by pressure from the solution containing the dextrose, then suspended in water, and decomposed by carbonic anhydride. On concentration of the filtered liquid, the lævulose is obtained as a colourless uncrystallisable syrup,

sweeter than dextrose. A solution of lævulose turns the polarised ray to the left and to a greater extent than dextrose turns the ray to the right, so that a mixture of equal proportions of dextrose and lævulose is lævorotatory: hence the name *invert-sugar* applied to the product of the hydrolysis of cane-sugar. The apparent specific rotatory power of lævulose rapidly diminishes, however, as the temperature of the solution rises, being nearly double as great at  $0^{\circ}$  as at about  $90^{\circ}$ , when it is about equal to that of dextrose;<sup>1</sup> the alteration in rotatory power is perhaps due to the gradual destruction of a hydrate as the temperature rises. Lævulose is more easily acted upon by dilute acids than dextrose, and is converted into acetopropionic or lævulinic acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ , when boiled with dilute sulphuric acid; dextrose yields only traces of this acid. It ferments in contact with yeast, though somewhat less readily than dextrose. Like dextrose, it yields saccharic acid on oxidation. Both dextrose and lævulose yield mannite when submitted to the action of nascent hydrogen.

LACTOSE,  $\text{C}_6\text{H}_{12}\text{O}_6$ .—On boiling an aqueous solution of milk-sugar to which a small quantity of sulphuric acid has been added, a mixture of ordinary dextrose and lactose is obtained. The properties of lactose have not yet been satisfactorily determined. It has a considerably higher apparent specific rotatory power than dextrose, but a slightly lower cupric reducing power. On oxidation with nitric acid, it yields mucic acid, the isomeride of saccharic acid; and dulcite, the isomeride of mannite, is formed on submitting it to the action of nascent hydrogen.

ARABINOSE or *Arabinodextrose*,  $\text{C}_6\text{H}_{12}\text{O}_6$ .—This glucose is obtained by hydrolysis of arabin (see p. 201). It crystallises in anhydrous rhombic prisms. Arabinose has a slightly

<sup>1</sup> A solution of invert-sugar containing 17.21 grams per 100 c.c. has at  $0^{\circ}$  the apparent specific rotatory power  $[\alpha]_D = -27^{\circ}.9$ , and the alteration in rotatory power as the temperature is raised is in accordance with the equation  $[\alpha]'_D = -(27^{\circ}.9 - .32t)$ , so that the solution should appear inactive at  $87^{\circ}.2$  (Tuschnid).



higher cupric reducing power than dextrose and a much higher specific rotatory power, viz.  $[\alpha]_D = 118^\circ$  in a solution containing 10 grams in 100 c.c. It does not ferment in contact with yeast.

INOSITOL or *Inosite*,  $C_6H_{12}O_6$ .—This carbohydrate occurs in the muscular substance of the heart, and in the lungs, kidneys, and liver; it has also been extracted from green beans and the unripe fruit of *Phaseolus vulgaris*. It crystallises in large rhombic plates of the composition  $C_6H_{12}O_6 \cdot H_2O$ ; it is optically inactive, without cupric reducing power, and it is not affected even by boiling with acids or alkalies. An aqueous solution does not ferment in contact with yeast, but it undergoes the lactic and butyric fermentation.

Little is known of Sorbinose or Sorbin and of Eucalyptodextrose or Eucalyn; they are distinguished, however, from the remaining members of the group by the circumstance that they do not undergo fermentation when mixed with yeast.

#### GROUP II. SACCHARONS: $C_{12}H_{22}O_{11}$ .

SACCHARON or *Cane-sugar*,  $C_{12}H_{22}O_{11}$ .—This carbohydrate is very widely distributed throughout the vegetable kingdom, but the two chief sources from which it is obtained are the sugar-cane (*Saccharum officinarum*), cultivated in various tropical countries, and the sugar-beet, which is largely cultivated in Europe, more especially in Germany and France.

Cane-sugar is exceedingly soluble in water, but sparingly soluble in alcohol; it crystallises from an aqueous solution on slow evaporation in anhydrous monoclinic prisms. Its apparent specific rotatory power varies only slightly with dilution, the value of  $[\alpha]_D$  for a solution containing 3.8 per cent. by weight being  $66^\circ.8$ , and for a solution containing 69.2 per cent.  $65^\circ.5$ ; the absolute specific rotatory power of cane-sugar, according to Tollens, is  $64^\circ.16$ . If heated for some time at about  $160^\circ$ , it is converted, without loss of



weight, into a mixture of dextrose and so-called lævulosan, a substance formed by the withdrawal of the elements of water from lævulose; if the heating be continued, water separates and caramel is produced, and on further heating a number of gaseous and liquid decomposition-products are formed, and ultimately a carbonaceous mass alone remains. Cane-sugar is at once decomposed by concentrated sulphuric acid, with separation of carbon; this behaviour serves to distinguish it from dextrose, which is not nearly so easily affected. It is, however, much less readily decomposed than dextrose on boiling with caustic alkalies; and it only very slowly and imperfectly reduces Fehling's solution even on prolonged boiling. Cane-sugar is not directly fermentable, but when its dilute aqueous solution is mixed with yeast, it is soon converted into a mixture of dextrose and lævulose, which then undergo the vinous fermentation. The hydrolysis of sugar may be effected even by prolonged boiling with water, but it occurs much more rapidly in the presence of acids.

Various metallic derivatives have been obtained from cane-sugar; it also yields a number of ethereal salts: thus, by heating with a large excess of acetic anhydride, it is converted into octacetosaccharon,  $C_{12}H_{14}O_{11}(C_2H_3O)_8$ .

It yields saccharic acid on oxidation.

AMYLON or *Maltose*,  $C_{12}H_{22}O_{11}$ .—This carbohydrate is the end-product of the action of diastase (malt extract) on starch. Amylon separates from 80 per cent. alcohol in crystalline crusts of the composition  $C_{12}H_{22}O_{11}.OH_2$ ; the anhydrous substance is extremely hygroscopic. It is readily acted on by Fehling's solution, but has only  $\frac{61}{100}$  of the reducing power of dextrose. In a 20 per cent. solution it has the apparent specific rotatory power  $[\alpha]_D = 139^\circ.3$  (Soxhlet). By prolonged warming with dilute acids, amylon is converted into dextrose.

LACTON or *Lactosaccharon* (*Milk-sugar*),  $C_{12}H_{22}O_{11}$ .—This sugar is an important constituent of milk, from which

it may be obtained by evaporating to a syrup the *whely* which remains after the separation of the casein, either by the addition of rennet or of a small quantity of acid, and purifying the crystals which slowly separate out by recrystallisation. It crystallises in hard, semi-transparent, rhombic prisms of the composition  $C_{12}H_{22}O_{11} \cdot OH_2$ , which may be rendered anhydrous by heating at  $130^\circ$ . Milk-sugar is far less soluble in water than cane-sugar, and has only a faint, sweet taste; it has almost the same constant apparent specific rotatory power as dextrose:  $[\alpha]_D = 53^\circ \cdot 12$  (strength of solution?) (Mills and Hogarth). Its cupric reducing power is about seven-tenths that of dextrose. It yields both mucic and saccharic acid on oxidation. As in the case of cane-sugar, vinous fermentation only takes place after its aqueous solution, mixed with yeast, has stood for some time, and the saccharon has undergone hydrolysis. In other respects, lacton closely resembles cane-sugar, but is on the whole a far more stable body.

According to Demole, if the mixture of lactose and dextrose obtained by hydrolysis of milk-sugar be boiled with acetic anhydride, an octacetate is obtained, having the formula  $C_{12}H_{14}O_{11}(C_2H_3O)_8$ , identical with that produced by the action of acetic anhydride on milk-sugar itself.

MYCON, LARIXON AND EUCALYPTON.—Mycon occurs in a large number of fungi, often in such quantity that it may be separated by mere extraction with alcohol. It is remarkable as being the most stable of the crystalline carbohydrates and as possessing the highest apparent specific rotatory power, viz.  $[\alpha]_D = 200^\circ$  in 5–6 per cent. solution. It appears to yield dextrose on hydrolysis.

Larixon is obtained from the saccharine exudation of the *Pinus larix*, and Eucalypton from a similar exudation from various species of Eucalyptus. Very little is known of these saccharons.

GROUP III. AMYLOIDS :  $C_{6n}H_{10n}O_{5n}$ .

This group comprises all those carbohydrates which, like starch, are represented by the empirical formula  $(C_6H_{10}O_5)_n$ . There is little doubt that  $n$  in this formula has not the same value for all the members of the group, but its value has not yet been determined for any one of them; probably it is in no case less than 4.

STARCH.—This carbohydrate is met with in more or less abundance in every plant and in most parts of plants; potato tubers, for example, containing from 20 to 27 per cent., and wheat from 50 to 75 per cent. It always occurs in the form of minute granules, which, however, differ in size and shape in different plants; these granules exhibit a concentrically stratified structure, due to their consisting of layers differing in density and the amount of water associated with the starch; they are coated with an extremely fine envelope of so-called starch-cellulose, a substance intermediate in its properties between starch and cellulose, which apparently is also distributed throughout the grain. Potato starch, purified by treating it successively with very dilute solution of potassic hydrate and 1 per cent. solution of hydrochloric acid, contains from 2 to 5.5 per cent. of starch cellulose, according to the amount of washing with alkali which it has received.

Ordinary commercial starch contains about 18 per cent. of water, part of which it loses on exposure over sulphuric acid in vacuo; it then corresponds in composition with the formula  $C_6H_{10}O_5.OH_2$ , but may be rendered anhydrous by drying at  $100^\circ$  in a current of air. Anhydrous starch may be heated at  $160^\circ$  without undergoing change, but at a slightly higher temperature it apparently suffers a somewhat complex decomposition, becoming completely soluble in water; when hydrated, it is much more easily altered by heat. Starch modified in this manner is known as torrefied starch or British gum, which is largely used as a thickener in calico printing. Starch is an extremely inert

substance. It is insoluble in alcohol and ether ; but it dissolves in potassic hydrate solution, in consequence of the formation of a potassium derivative. On heating with acetic anhydride, it is converted into a triacetate,  $C_6H_7O_2(C_2H_3O_2)_3$ . It is without cupric reducing power. It has a high apparent specific rotatory power in solution.

Starch grains when intact are unacted on by cold water, but if heated with water to a temperature which varies from  $45^{\circ}$ – $90^{\circ}$  for different varieties, the grains absorb water, swell enormously and ultimately burst, forming an opalescent viscous solution often termed starch paste. The solution is coloured a magnificent blue on the addition of even traces of iodine. If heated with water at about  $150^{\circ}$ , starch is converted into so-called soluble starch, which is also coloured blue by iodine, but distinguished from starch by readily dissolving in water at  $70^{\circ}$  to form a perfectly limpid solution.

Starch undergoes a most remarkable series of transformations under the influence of the diastase of malt extract. If sufficient malt extract be added to a cold 3 to 4 per cent. starch paste, complete limpidity ensues within from three to four minutes, the starch being converted into soluble starch ; at this point iodine produces a deep indigo-blue coloration, but as the change proceeds iodine causes at first a violet and then a deep reddish-brown colour, and after very few minutes ceases to have any effect. From the product thus obtained, two substances may be isolated : one a carbohydrate of the same empirical composition as starch, called dextrin (amylon) ; the other, an isomeride of cane-sugar, termed maltose (amylon). The former is a white amorphous substance easily soluble in water, but almost insoluble in alcohol ; like starch, it is without cupric reducing power. The apparent specific rotatory powers of amylin and amylin being known as well as the cupric reducing power of the former, it would appear from the cupric reducing power and apparent specific rotatory power of the solutions obtained by acting with malt extract on starch under various condi-

tions that the following are the changes which occur. When the action takes place in the cold, or at temperatures not exceeding  $60^{\circ}$ , the relative amounts of amylon and amylin produced are in accordance with the equation  $(C_6H_{10}O_5)_{20} + 8OH_2 = 8C_{12}H_{22}O_{11} + (C_6H_{10}O_5)_4$ . If the malt extract be heated to  $66^{\circ}$ , a much smaller proportion of amylon is formed, viz.  $3C_{12}H_{22}O_{11} : (C_6H_{10}O_5)_{14}$ ; if it be heated to  $75^{\circ}$ , or if malt extract heated to  $66^{\circ}$  and rendered alkaline with sodic carbonate be employed, the proportions are  $2C_{12}H_{22}O_{11} : (C_6H_{10}O_5)_{16}$ ; and, lastly, if the transformation be effected by malt extract heated to  $66^{\circ}$  and made very slightly alkaline with sodic hydrate, the minimum proportion of amylon, viz.  $C_{12}H_{22}O_{11} : (C_6H_{10}O_5)_{18}$ , is obtained. There is some evidence that other intermediate products, partaking of the nature both of amylon and amylin, are also formed besides amylon and amylin.

These remarkable results may be explained on the assumption that soluble starch has a very complex formula, viz.  $C_{120}H_{200}O_{100} = (C_6H_{10}O_5)_{20}$ , and that the amylin produced under various conditions are not identical but polymeric substances. This hypothesis cannot, however, at present be regarded as established, but is extremely suggestive.

The amylin is more or less gradually acted upon by malt extract and converted into amylon; this latter, however, is not affected by diastase, although cane-sugar is slowly hydrolysed by it. Starch apparently undergoes a similar series of changes when submitted to the action of dilute sulphuric acid, but is finally resolved into ordinary dextrose. Saliva resembles malt extract in its action on starch, but is said to produce a small quantity of dextrose. The pancreatic secretion readily converts starch into amylin and amylon, and also slowly converts the latter into dextrose; but it is entirely without action on cane-sugar. The secretion of the small intestine, on the other hand, has only a feeble action on starch, but rapidly hydrolyses amylon and also hydrolyses cane-sugar, although only to a limited extent. (Brown and Heron.)



INULIN ( $C_6H_{10}O_5$ )<sub>n</sub>.—This carbohydrate is found in the tubers of *Inula helenium*, *Helianthus tuberosus*, *Dahlia*, and other *Compositæ*, and may be obtained by washing the rasped root with water, and allowing the inulin to settle down from the liquid. It is a white, amorphous, and tasteless substance, insoluble, or nearly so, in cold water, but readily soluble in boiling water. The solution is coloured brown by iodine.

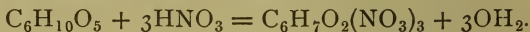
Inulin apparently bears somewhat the same relation to lævulose that the amylin bears to dextrose, since it is ultimately converted into lævulose by boiling with dilute acids.

GLYCOGEN, ( $C_6H_{10}O_5$ )<sub>n</sub>, is a substance of the same percentage composition as starch, which occurs chiefly in the liver of various animals. It may be extracted by boiling with water and precipitated by the addition of alcohol. Glycogen is a white amorphous tasteless body; it dissolves in water forming an opalescent solution, which is coloured violet or brown-red by iodine; it does not reduce an alkaline cupric solution, nor does it ferment in contact with yeast, but it is converted into dextrose on boiling with diluted sulphuric acid, or when placed in contact with diastase, saliva, or pancreatic fluid, amylon and amylin being formed as intermediate products.

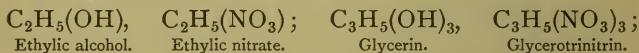
CELLULOSE ( $C_6H_{10}O_5$ )<sub>n</sub>.—Cellulose is the main constituent of the cells of which all vegetable structures are built up; thus cotton is almost pure cellulose. Cellulose is colourless and transparent; it is insoluble in water, alcohol, and all ordinary solvents, but is dissolved by a solution of cupric hydrate in ammonia, from which it is reprecipitated on the addition of acids in the form of white flocculi. Iodine does not colour it. If cellulose be placed in cold concentrated sulphuric acid, it is at first converted into a jelly-like substance which after a time dissolves; if much water be then added, and the solution heated for some hours, care being taken to replace the water as it evaporates, the cellulose is ultimately entirely converted into dextrose. Linen rags, for example, thus treated, furnish more than their own weight of dextrose.



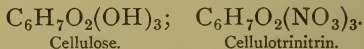
When acted upon by a mixture of concentrated nitric and sulphuric acids, cellulose yields a variety of nitrates (*cellulose nitrins*), all more or less explosive, the nature of which depends on the strength of the acids employed and the length of time during which the cellulose is in contact with the acid mixture. Thus, if purified cotton-wool be steeped for some hours in a mixture of one volume nitric acid (sp. gr. 1.5) with three volumes concentrated sulphuric acid, it increases greatly in weight, and is converted, without undergoing any change of form or in appearance, into *pyroxylin* or *gun-cotton* (*cellulotrin*), the reaction which occurs being represented by the equation :



The compound so produced bears to cellulose exactly the same relation that ethylic nitrate bears to ethylic alcohol, or that glycerotrinitrin (nitroglycerin) bears to glycerin :

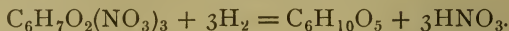


cellulose being a trihydric alcohol, of which pyroxylin is the normal nitrate :



Pyroxylin is insoluble in water, alcohol, and ether, but by employing less concentrated nitric acid, lower nitrates are produced, which are soluble in a mixture of alcohol and ether. A solution of these compounds in a mixture of alcohol and ether constitutes the well-known *collodion*.

The cellulonitrins thus formed are all reconverted into cellulose by the action of reducing agents :



**GUMS.**—The gums are a class of substances of vegetable origin, more or less closely related to the sugars ; many of them dissolve in water, but are precipitated on the addition of alcohol, while others merely swell up owing to the absorption of water and do not dissolve. Some are of the same

percentage composition as cane-sugar, and others appear to be of the same composition as starch; but we possess little certain knowledge on this point, owing to the difficulty which exists of obtaining pure substances, most of the gums being more or less complex mixtures.

The best known of the gums is *gum arabic*, the dried exudation from various species of *acacia* growing in Arabia and Egypt, which is usually met with in the form of colourless or yellowish non-crystalline brittle masses, soluble in water. Gum arabic is not a pure substance, however, since on incineration it yields 3-4 per cent. of ashes consisting chiefly of potassic, magnesian, and calcic carbonate; moreover, specimens from different sources, when dissolved in water, do not affect a ray of polarised light to the same degree, some causing a rotation more or less to the left, others a rotation to the right. The main constituent of gum arabic is termed *arabin*, which is said to be a compound of the formula  $C_{12}H_{22}O_{11}$ , but this appears doubtful. The gum which oozes from chinks in the bark of cherry and plum trees contains, together with arabin, a considerable proportion of an insoluble modification termed *metarabin*, which merely swells up to a jellylike mass when placed in water, but on treatment with alkalis is rapidly rendered soluble and converted into arabin. Arabin and metarabin appear to be normal constituents of most plants, the latter being especially plentiful in the sugar-beet, which in some seasons also contains a considerable proportion of arabin in its sap. Arabin is soluble in water so long as it is kept moist, but when once dried it ceases to dissolve, and merely swells up in water; basic plumbic acetate produces in the aqueous solution to which ammonia has been added a white precipitate which is said to have the composition  $C_{12}H_{20}PbO_{11}$ .

On heating arabin with diluted sulphuric acid, a crystalline isomeride of dextrose, *arabinose*,  $C_6H_{12}O_6$ , is obtained, together with a non-crystalline dextrorotatory carbohydrate which apparently is fermentable. On treatment of different specimens of gum arabic with diluted sulphuric acid, ara-

binose and the non-crystalline carbohydrate are obtained in varying proportions; the arabin separated from the sugar-beet yields on hydrolysis a proportionately larger quantity of arabinose, so that it is probable that gum arabic and arabin from sugar-beet are mixtures in different proportions of the same two compounds, one of which is strongly lævoro-rotatory and convertible into arabinose, the other being dextrorotatory and convertible into a non-crystalline carbohydrate, this latter being predominant in most specimens of gum arabic.

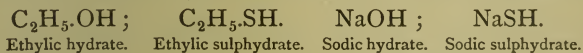
The roots of the mallow and of various species of orchis, linseed, and in fact most plants, contain mucilaginous substances, all of which yield mucic acid on oxidation, and which are apparently closely related to gum arabic. The so-called *pectous* substances probably also belong to the class of carbohydrates.

*Constitution of the carbohydrates.*—The determination of the constitution of the carbohydrates mainly rests on the facts, (1) that, when submitted to the action of nascent hydrogen, the glucoses dextrose and lævulose are converted into mannite, lactose yielding the isomeric alcohol dulcitol; (2) that these hex-hydric alcohols are both derivatives of the paraffin normal hexane,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ , as shown by their conversion into the iodo-hexane,  $\text{C}_4\text{H}_9\cdot\text{CHI}\cdot\text{CH}_3$ , by the action of hydriodic acid; and (3) that dextrose and lævulose yield saccharic acid,  $\text{COOH}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{COOH}$ , and lactose the isomeric mucic acid on oxidation. On account of their stability, mannite and dulcitol cannot well be represented except by formulæ in which each hydroxyl (OH) group is shown to be associated with a different carbon symbol; but from normal hexane only one formula can be derived, viz.  $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2(\text{OH})$ , which satisfies this condition: hence it would seem that the ordinary hypothesis that isomerides are bodies having different rational formulæ is insufficient to explain the isomerism of the alcohols in question, and that the nature of the relation which they bear to each other remains to be discovered. The same apparently is true of the glucoses and perhaps even of the saccha-

rons. The simplest explanation of the properties of the glucoses would appear to be furnished by the assumption that they are all penthydic monaldehydes, and that they have in common the formula  $\text{CH}_2(\text{OH}).\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{COH}$ . The saccharons may be regarded as related to the glucoses somewhat in the same manner that ethylic ether and alcohol are related, i.e. as bodies of the formula  $[\text{COH}.C_5H_6(\text{OH})_4]_2O$ ; but it may be objected that the fact that cane sugar and other saccharons are not acted upon by Fehling's solution is scarcely compatible with the assumption that these carbohydrates are aldehydic compounds, i.e. contain the group  $\text{COH}$  in their formulæ. Fehling's solution, however, is not to be compared with an ordinary oxidising agent—most of which act upon the carbohydrates generally—and there is no reason to believe that the reducing power of the glucoses is to be attributed to the  $\text{COH}$  group. There is little to indicate the constitution of the remaining carbohydrates. The simplest of the 'amylin's' from starch, supposing several to exist, is not improbably a body of the formula  $C_{24}H_{40}O_{20} = 4C_6H_{10}O_5$ , formed from the corresponding saccharon in the same way that the latter is from the corresponding glucose. Starch and many of the amyloids are very probably in a measure analogous in constitution to compounds such as the polymerides of aldehyde (p. 225).

#### MERCAPTANS OR THIO-ALCOHOLS.

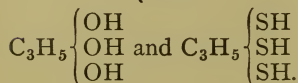
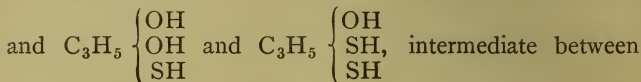
The relation which these compounds bear to the alcohols is of precisely the same character as the relation which exists between the metallic sulphydrates and the metallic hydrates:



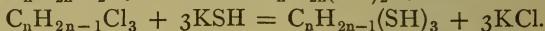
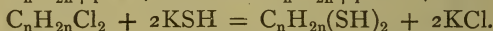
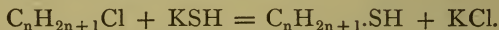
Mercaptans corresponding to the monohydric alcohols of the  $C_nH_{2n+1}.OH$ ,  $C_nH_{2n-1}.OH$ , and  $C_nH_{2n+7}.OH^1$  series; to

<sup>1</sup> This series includes compounds of two classes, which correspond respectively to the phenols and to benzylic alcohol and its homologues. The mercaptans of the former class (*thiophenols*) cannot be prepared by the action of metallic sulphydrates on the haloid derivatives of the corresponding hydrocarbons; but those of the latter class are readily obtained from the mono-haloid derivatives formed by the action of chlorine or bromine on the boiling hydrocarbons homologous with benzene.

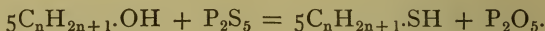
the dihydric alcohols of the  $C_nH_{2n}(OH)_2$  and  $C_nH_{2n-8}(OH)_2$  series ; and to the trihydric alcohols of the  $C_nH_{2n-1}(OH)_3$  series, are known. Several compounds, intermediate between the alcohols and mercaptans have been obtained ; such as



*General Methods of Formation.*—1. By the action of potassic sulphhydrate on haloid derivatives of the hydrocarbons of the  $C_nH_{2n+2}$  and  $C_nH_{2n}$  series, thus :



2. By distillation of the corresponding alcohols with phosphorus pentasulphide, e.g. :



This method has hitherto only been applied to the preparation of mercaptans corresponding to monohydric alcohols of the  $C_nH_{2n+1}.OH$  and  $C_nH_{2n-7}.OH$  series, but is doubtless of general application.

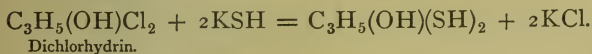
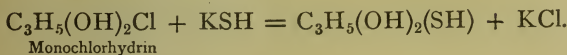
3. By the action of nascent hydrogen on the acid chlorides derived from the sulphonic acids, for example :



This method appears to be generally available.



4. The mode of preparing the compounds intermediate between the alcohols and mercaptans will be evident from the following examples :



*Properties.*—The mercaptans of the  $\text{C}_n\text{H}_{2n+1}\cdot\text{SH}^1$  and  $\text{C}_n\text{H}_{2n-1}\cdot\text{SH}$  series are mobile colourless liquids ; those of the  $\text{C}_n\text{H}_{2n}(\text{SH})_2$  and  $\text{C}_n\text{H}_{2n-1}(\text{SH})_3$  are viscid liquids which undergo alteration on distillation ; the first term of the  $\text{C}_n\text{H}_{2n-7}\cdot\text{SH}$  series (*Thiophenol*,  $\text{C}_6\text{H}_5\cdot\text{SH}$ ) is a liquid, but its homologues are mostly crystalline. The only known member of the  $\text{C}_n\text{H}_{2n-8}(\text{SH})_2$  series (*Thioresorcin*,  $\text{C}_6\text{H}_4(\text{SH})_2$ ) is a crystalline solid. Nearly all the mercaptans possess offensive alliaceous odours. The mercaptans yield metallic derivatives analogous to those obtained from the alcohols. These derivatives are bodies of considerable stability, and many of them are readily obtained in a crystalline condition ; they are formed from the mercaptans by the action of metals, such as sodium and potassium, or of metallic oxides, such as mercuric oxide,<sup>2</sup> or by the addition of metallic salts, such

<sup>1</sup> The following mercaptans of the  $\text{C}_n\text{H}_{2n+1}\cdot\text{SH}$  series have been obtained :

|                       |                                         | B.-P.                       |
|-----------------------|-----------------------------------------|-----------------------------|
| Methylic sulphhydrate | $\text{CH}_3\cdot\text{SH}$             | $21^\circ$                  |
| Ethylic           ,,  | $\text{C}_2\text{H}_5\cdot\text{SH}$    | $36^\circ$                  |
| Isopropylic     ,,    | $\text{C}_3\text{H}_7\cdot\text{SH}$    | $57^\circ\text{--}60^\circ$ |
| Isobutylic*    ,,     | $\text{C}_4\text{H}_9\cdot\text{SH}$    | $88^\circ$                  |
| Isoamyllic*    ,,     | $\text{C}_5\text{H}_{11}\cdot\text{SH}$ | about $120^\circ$           |

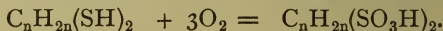
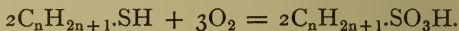
\* These are derived from the alcohols of fermentation.

<sup>2</sup> The name mercaptan (from *corpus mercurio aptum*), which has now become generic, was originally applied to the first-discovered member of the class (ethylic sulphhydrate,  $\text{C}_2\text{H}_5\cdot\text{SH}$ ) on account of the energetic reaction which occurs when it is brought in contact with mercuric oxide.



as plumbic acetate and mercuric chloride, to their alcoholic solutions.

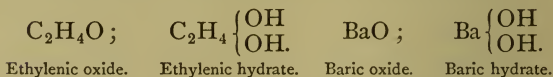
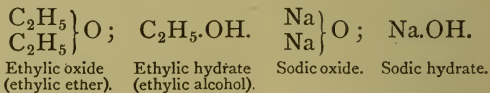
Most characteristic of the mercaptans, however, is their behaviour on oxidation by nitric acid, whereby they are ultimately converted into sulphonic acids, thus :



## CHAPTER VII.

### ETHERS.

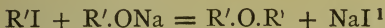
THE ethers are a class of compounds bearing to the alcohols precisely the same relation that the metallic oxides bear to the metallic hydrates ; they may, in fact, conveniently be regarded as oxides of radicles of which the alcohols may be considered to be the hydrates, thus :



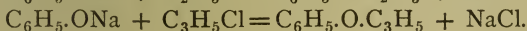
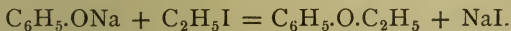
*General Methods of Preparation.* — The ethers of the  $(\text{C}_n\text{H}_{2n+1})_2\text{O}$ ,  $(\text{C}_n\text{H}_{2n-1})_2\text{O}$  and  $(\text{C}_n\text{H}_{2n-7})_2\text{O}$  series, corresponding to the monohydric alcohols of the ethylic, allylic, and benzylic series, are obtained by the action of the mono-haloid derivatives<sup>1</sup> of the corresponding hydrocarbons on the

<sup>1</sup> Only such mono-haloid derivatives as are convertible into, or are derived from, corresponding alcohols are available, however. For example, the monochloropropylene (allylic chloride) derived from allylic

sodium or potassium derivatives of the corresponding alcohols, e.g. :



If the mono-haloid derivative taken is derived from, or convertible into, an alcohol identical with that from which the metallic derivative employed is formed, so-called *simple ethers* are obtained ; if it is derived from, or convertible into, an isomeric, homologous, or isologous alcohol, so-called *mixed ethers* are produced. Thus by the action of ethylic iodide (iodethane) on sodic ethylate ( $C_2H_5I + C_2H_5.ONa = NaI + C_2H_5.O.C_2H_5$ ) the simple ether, *ethylic oxide* is obtained, which is metameric with the mixed ether, *propylic methylic oxide*,  $(C_3H_7)^\alpha O.CH_3$ , formed by the action of propylic iodide ( $\alpha$ -iodopropane) on sodic methylate, and with the isomeric ether *isopropylic methylic oxide*,  $(C_3H_7)^\beta O.CH_3$ , from isopropylic iodide ( $\beta$ -iodopropane). Similarly, by the action of the mono-haloid derivatives of the paraffins on the metallic derivatives of allylic alcohol, or by the action of allylic chloride, bromide, or iodide on the sodium or potassium derivatives of the monohydric alcohols derived from the paraffins, a series of mixed ethers of the form  $C_nH_{2n+1}.O.C_3H_5$  are obtained. Other series of mixed ethers are produced by the action of the mono-haloid derivatives corresponding to the alcohols of the ethylic, allylic, and benzylic series on the sodium derivatives of the phenols, e.g.:

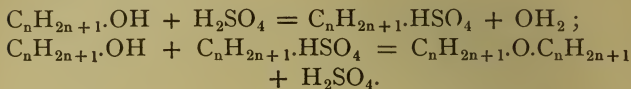


A second general method of preparing simple and mixed

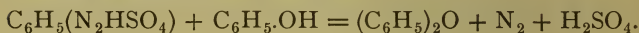
alcohol readily lends itself to this reaction, but the isomeric monochloropropylene which is the first product of the action of potassic hydrate on dichloropropane, and which cannot be converted into a corresponding alcohol, is resolved into allylene and hydrochloric acid.

<sup>1</sup> In this equation R denotes a radicle of the  $C_nH_{2n+1}$ ,  $C_nH_{2n-1}$ , or  $C_nH_{2n-7}$  series.

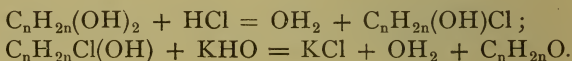
ethers corresponding to the alcohols of the ethylic and allylic series consists in acting upon the acid ethereal salts formed from the alcohols and sulphuric acid with the alcohols of these series, thus :



Neither of the above methods is available for the preparation of ethers corresponding to the phenols. Only one such compound is known, *phenylic ether*, obtained by fusing phenol with diazobenzene sulphate :



The ethers corresponding to the dihydric alcohols, the glycols, are prepared by the withdrawal of hydrochloric acid, by the action of potassic hydrate, from the chlorhydrins formed from these alcohols by the action of hydrochloric acid :



Numerous mixed ethers are obtained by the action of mono-haloid hydrocarbon derivatives on the sodium derivatives of the glycols, e.g. :

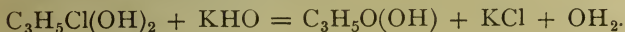


The ether of the trihydric alcohol glycerin is obtained, together with other products, on heating glycerin with calcic chloride :



It is a colourless somewhat thick liquid. A compound intermediate between this glyceric ether and glycerin, bearing to them the same relation that bismuthous hydrate,  $\text{BiO}(\text{OH})$ , bears to bismuthic oxide,  $\text{Bi}_2\text{O}_3$ , and to bismuthic hydrate,

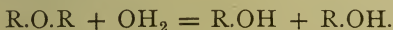
$\text{Bi}(\text{OH})_3$ , is produced by acting upon the monochlorhydrin of glycerin with potassic hydrate :



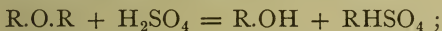
Numerous mixed ethers have been obtained by the action of the chlorhydrins of glycerin on the sodium-derivatives of the alcohols of the ethylic and allylic series.

Little is known of the ethers of other series than the above-mentioned.

*General Properties of the Ethers.*—The simple and mixed ethers derived from the monohydric alcohols of the ethylic and allylic series are colourless mobile liquids. By prolonged heating with water they are resolved into their generators, the alcohols :



On digesting them with concentrated sulphuric acid the corresponding acid ethereal sulphates are produced :



They are similarly decomposed on heating with concentrated aqueous solutions of the haloid acids :



and by the action of phosphoric chloride :



The mixed ethers of the form  $\text{C}_n\text{H}_{2n-7}.\text{O}.\text{C}_n\text{H}_{2n+1}$ <sup>1</sup> derived from the phenols behave somewhat differently. They are decomposed by the haloid acids (most readily by hydriodic acid) in the manner represented by the equation :



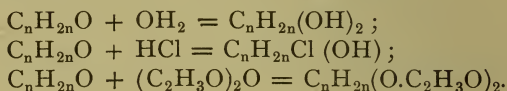
<sup>1</sup> These are generically termed *anisols*, the first member of the series,  $\text{CH}_3.\text{O}.\text{C}_6\text{H}_5$ , having received the name *anisol* on account of its formation from anisic acid.

and on treating with concentrated sulphuric acid are converted into sulphonic acids :



The ethers derived from the phenols appear to be still more stable compounds. Thus phenylic ether (a crystalline compound melting at  $28^\circ$  and distilling at  $248^\circ$ ) is not affected by heating with a concentrated aqueous solution of hydriodic acid to  $250^\circ$  ; concentrated sulphuric acid converts it into the disulphonic acid  $(C_6H_4.HSO_3)_2O$ .

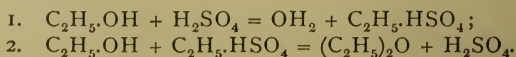
The ethers derived from the glycols are far less inert compounds than the ethers derived from the monohydric alcohols ; they combine with water (to reproduce the glycols), the haloid acids, acetic anhydride, &c., thus :



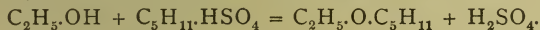
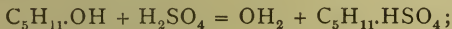
These changes are readily effected by gently heating the ethers with the respective reagents in closed vessels.

ETHYLIC OXIDE (*Ethylic Ether*, *Ether*),  $C_4H_{10}O = (C_2H_5)_2O$ .—*Preparation*.—On the large scale ether is always prepared by the so-called continuous process :—

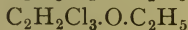
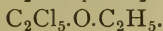
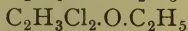
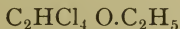
A mixture of 5 parts of 90 per cent. alcohol with 9 parts of concentrated sulphuric acid is heated to a temperature of  $140^\circ$ – $145^\circ$  in a vessel provided with an efficient condenser, and a constant stream of alcohol allowed to flow in, the rate of flow being so regulated as to maintain the temperature at about  $140^\circ$ . Water and ether distil over together, the formation of the latter being the result of two separate and successive changes : the alcohol is in the first instance converted into hydric ethylic sulphate (sulphovinic acid), which by the action of a further quantity of alcohol is converted into ether and sulphuric acid, thus :



The acid thus liberated again enters into reaction with alcohol, and is again liberated, and this cycle of changes is repeated over and over again. Theoretically the same quantity of acid should convert an unlimited quantity of alcohol into ether; practically, however, this is not the case,<sup>1</sup> partly in consequence of the retention of water by the acid which thus becomes too dilute to etherify the alcohol, partly in consequence of the occurrence of carbonisation and oxidation at the expense of the sulphuric acid. If, in the first place, a mixture of some other alcohol than the ethylic with sulphuric acid be taken and ethylic alcohol be then added gradually, a mixed ether is produced; thus, supposing amylic alcohol be taken, ethylic amylic ether is obtained :



*Properties.*—Ethylic oxide is a colourless very mobile liquid, having a peculiar exhilarating odour; it is very volatile, boiling at  $35^\circ.5$ —the vapour forms a highly explosive mixture with air; it is somewhat soluble in water, and miscible in all proportions with alcohol. Ethylic oxide combines with bromine, with evolution of heat, forming a crystalline compound  $(\text{C}_4\text{H}_{10}\text{OBr}_3)_2$ , which is decomposed by water into its generators. By the action of chlorine on ethylic oxide a series of substitution-products is obtained, namely :



By the prolonged action of chlorine in sunshine it is ultimately converted into the perchlorinated derivative,  $\text{C}_2\text{Cl}_5\cdot\text{O}\cdot\text{C}_2\text{Cl}_5$ . The homologous ethers <sup>2</sup> closely resemble ethylic oxide.

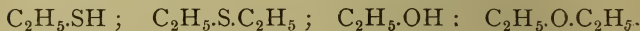
<sup>1</sup> The 9 parts of acid suffice to convert about 35 parts of alcohol into ether.

<sup>2</sup> The following ethers derived from normal primary alcohols of the ethylic series are known :—



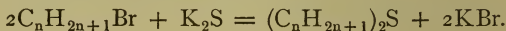
## THIO-ETHERS.

Whereas the ethers are the analogues of the metallic oxides, the thio-ethers are the analogues of the metallic sulphides: they bear the same relation to the mercaptans or thio-alcohols that the ethers bear to the alcohols:

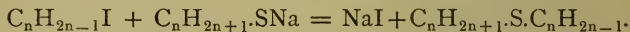


Thio-ethers have been obtained by the following general methods:—

1. By the action of mono-haloid derivatives of the hydrocarbons of the  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{C}_n\text{H}_{2n}$ , and  $\text{C}_n\text{H}_{2n-6}$ <sup>1</sup> series on potassic or sodic sulphide, e.g.:

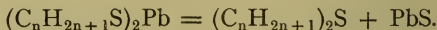


2. By the action of mono-haloid derivatives of the hydrocarbons of the  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{C}_n\text{H}_{2n}$ , and  $\text{C}_n\text{H}_{2n-6}$ <sup>1</sup> series on the sodic or potassic derivatives of the mercaptans, e.g.:



This method is applicable to the formation of mixed thio-ethers corresponding to the anisols from thiophenols.

3. By distillation of the lead derivatives of the mercaptans:

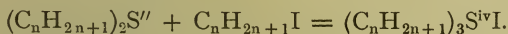


|                          |                                                                                                |        |
|--------------------------|------------------------------------------------------------------------------------------------|--------|
|                          |                                                                                                | B.-P.  |
| Methylic ether . . .     | $\text{C}_2\text{H}_6\text{O} = \text{CH}_3\cdot\text{O}\cdot\text{CH}_3$                      | −21°   |
| Methylic ethylic ether . | $\text{C}_3\text{H}_8\text{O} = \text{CH}_3\cdot\text{O}\cdot\text{C}_2\text{H}_5$             | +11°   |
| Ethylic ether . . .      | $\text{C}_4\text{H}_{10}\text{O} = \text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ | 35°.5  |
| Methylic propylic ether  | $\text{C}_5\text{H}_{12}\text{O} = \text{CH}_3\cdot\text{O}\cdot\text{C}_3\text{H}_7$          | 49–52° |
| Ethylic propylic ether . | $\text{C}_5\text{H}_{12}\text{O} = \text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_3\text{H}_7$ | 68–70° |
| Propylic ether . . .     | $\text{C}_6\text{H}_{14}\text{O} = \text{C}_3\text{H}_7\cdot\text{O}\cdot\text{C}_3\text{H}_7$ | 85–86° |
| Butylic ether . . .      | $\text{C}_8\text{H}_{18}\text{O} = \text{C}_4\text{H}_9\cdot\text{O}\cdot\text{C}_4\text{H}_9$ | 141°   |

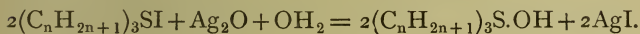
<sup>1</sup> The chlorinated and brominated derivatives of toluene and its homologues obtained by the action of chlorine or bromine on the boiling hydrocarbons are alone available.

This method is available for the preparation of simple thio-ethers from the thiophenols ; in fact, it is generally applicable whenever the thio-ether to be produced is capable of being distilled unchanged.

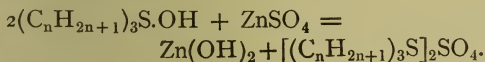
*General Properties.*—With few exceptions the thio-ethers are colourless or yellow liquid bodies, possessing characteristic offensive odours. The thio-ethers of the  $(C_nH_{2n+1})_2S$  and  $(C_nH_{2n-1})_2S$  series unite directly with the moniodo-paraffins and olefines obtained by the action of hydriodic acid on the alcohols of the ethylic and allylic series, to form a remarkable series of crystalline compounds ; e.g. :



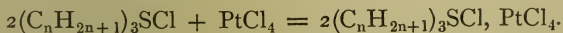
These compounds are converted by the action of moist argentic oxide into the corresponding hydrates :



These hydrates closely resemble the metallic hydrates ; their aqueous solutions are strongly caustic, exhibit an alkaline reaction, and precipitate metallic hydrates from solutions of metallic salts, thus :



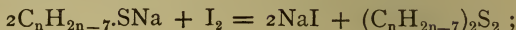
The corresponding chlorides form crystalline double salts with platinic chloride :



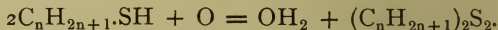
On oxidation the thio-ethers are directly converted into compounds of the form  $R_2SO$ , or  $R_2SO_2$  ; the ethers of the  $(C_nH_{2n+1})_2S$  and  $(C_nH_{2n-1})_2S$  series yielding compounds of both classes, whilst the ethers of the  $(C_nH_{2n-7})_2S$  series derived from the thiophenols appear to yield only compounds of the latter class.

Analogues of the metallic disulphides  $R'_2S_2$  are obtained

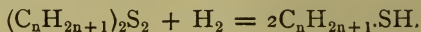
by the action of the halogens on the metallic derivatives of the mercaptans, e.g. :



and by careful oxidation of the mercaptans :



These sulphides are reconverted into mercaptans by the action of nascent hydrogen :



## CHAPTER VIII.

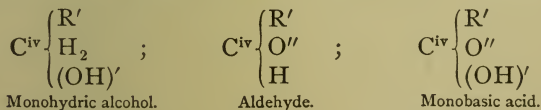
### ALDEHYDES.

THE aldehydes are a class of compounds intermediate between the *primary* alcohols and the corresponding acids, and are formed from the alcohols by the simple withdrawal of hydrogen—hence the name aldehyde, which is an abbreviation of *alcohol dehydrogenatum*. The monohydric primary alcohols are converted into the corresponding aldehydes by the withdrawal of two units of hydrogen ; the dihydric by the withdrawal of four units ; in short, a primary alcohol which is *n*-hydric is converted into the corresponding aldehyde by the withdrawal of *2n* units of hydrogen. The aldehydes are the first products of the oxidation of the primary alcohols ; they are characterised and distinguished from the ketones, which are similarly related to the secondary alcohols, by the fact that they are converted on oxidation into acids containing the same number of units of carbon, the change consisting in the assumption of an amount of

oxygen equivalent to the amount of hydrogen withdrawn in the formation of the aldehyde from the primary alcohol :



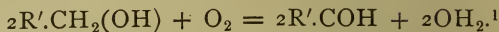
The methods employed in the formation of the primary monohydric alcohols, and their behaviour with reagents, have led to their representation by the general expression  $\text{R}.\text{CH}_2(\text{OH})$ , R being a monad hydrocarbon group or radicle ; in other words, the group  $(\text{CH}_2.\text{OH})$  is regarded as common to the monohydric primary alcohols ; similarly, the polyhydric primary alcohols, which are  $n$ -hydric, are formulated as containing the group  $(\text{CH}_2.\text{OH})$   $n$  times. On the other hand, a consideration of the reactions giving rise to the formation of aldehydes and their chemical behaviour, has led to the assumption that in the conversion of the primary alcohols into aldehydes, the group  $(\text{CH}_2.\text{OH})$  is alone affected, and is converted into the group  $(\text{COH})$ . Hence the aldehydes derived from monohydric alcohols are generally represented by the expression  $\text{R}'.\text{COH}$ , and the monobasic acids formed from them by oxidation by the formula  $\text{R}'.\text{CO}(\text{OH})$  ; the relation between the three series of compounds, as a comparison of the following general formulæ will show, is thus of an extremely simple character :



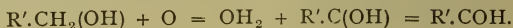
At present we are only acquainted with aldehydes derived from monohydric and dihydric alcohols ; those corresponding to the more important lower terms of the  $\text{C}_n\text{H}_{2n+1}.\text{OH}$ ,  $\text{C}_n\text{H}_{2n-1}.\text{OH}$ , and  $\text{C}_n\text{H}_{2n-7}.\text{OH}$  series of monohydric alcohols have been chiefly studied, and we have little or no knowledge of the higher terms of the series.

ALDEHYDES OF THE COMPOSITION  $R'.COH$ .

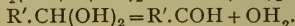
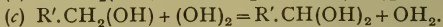
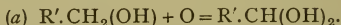
*General Methods of Formation.*—1. By the oxidation of the primary alcohols :



<sup>1</sup> It is usually supposed that the change which occurs on oxidation of the alcohols consists simply in the withdrawal of  $H_2$  from the  $CH_2(OH)$  group and the simultaneous resolution of the monad  $(OH)$  group into its constituents, thus :

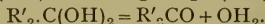
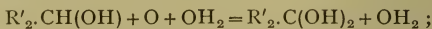


There is some probability, however, attaching to the assumption that the formation of the aldehyde is the result of two distinct changes, the first of which consists in the production of a compound of the form  $R'.CH(OH)(OH)$ , which is subsequently broken up into the aldehyde and water, the former of these changes being brought about either (a) by the direct addition of oxygen to the alcohol, or (b) by the combined influence of the nascent oxygen and water, or (c) perhaps by the agency of hydroxyl (hydric peroxide,  $(OH)_2$ ) itself, thus :



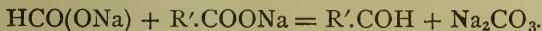
In support of this hypothesis is the fact that the aldehydes are known to form unstable compounds with water of the composition  $R'.CH(OH)_2$ , which are readily broken up into the aldehyde and water.

The same applies to the secondary alcohols which yield ketones on oxidation (see p. 149, and ketones), thus :



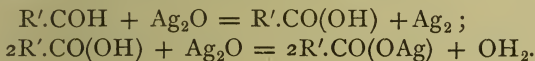
In the case of the tertiary alcohols,  $R'_3.C(OH)$  (see p. 149), the first change possibly consists in the resolution of the alcohol into a compound of the form  $R'_2.C(OH)_2$ , which is subsequently resolved into a ketone and water, and an alcohol of the form  $R'.OH$  which at once undergoes further oxidation. Thus in the case of dimethylisopropylcarbinol, which yields acetone and acetic acid on oxidation, the reaction may be resolved into the following phases :

2. By dry distillation of an intimate mixture of calcic, potassic, or sodic formate and the corresponding metallic salt of a monobasic acid :

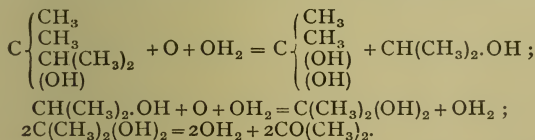
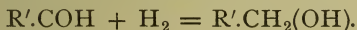


*General Properties.*—1. The aldehydes exhibit a remarkable tendency to suffer change, and, as a rule, can only be preserved unaltered for any length of time if perfectly pure ; the presence of mere traces of impurity often suffices to ensure their gradual conversion, either into polymeric substances, or condensation-products (see *acetic aldehyde*).

2. The aldehydes are readily converted by oxidation into corresponding acids, often by mere exposure to the air. In all cases this change is rapidly effected on warming with argentic oxide and water : metallic silver is deposited, the silver salt of the acid remaining in solution :



3. By the action of nascent hydrogen<sup>1</sup> the aldehydes are converted into the corresponding monohydric alcohols :



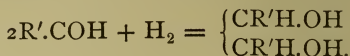
The acetic acid produced results from the oxidation of the acetone.

This example, moreover, is a striking illustration of the law which appears to govern these changes, viz. : that if the tertiary alcohol which is oxidised contain dissimilar groups, the ketone which is formed always contains the two most stable—usually the least complex—groups, the least stable—usually the most complex—group being split off and at once further oxidised.

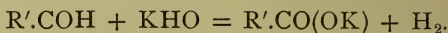
<sup>1</sup> The hydrogen evolved by the action of metals on diluted acids is not generally available for this purpose ; usually sodium amalgam is added to a solution of the aldehyde in water.



Often the fixation of hydrogen is accompanied by condensation, and a dihydric alcohol is also produced, thus :

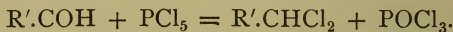


4. When heated with fused potassic hydrate, the aldehydes are converted into the potassic salts of the corresponding acids :

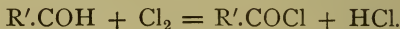


In many cases the hydrogen thus set free reacts at the moment of liberation on a portion of the aldehyde, and converts it into the corresponding alcohol (see p. 170).

5. By the action of phosphorus pentachloride or bromide, the oxygen of aldehydes may be replaced by the equivalent amount of chlorine or bromine, thus :



6. By the action of chlorine, when certain precautions are observed, the aldehydes are converted into the corresponding acid chlorides (see *acetic aldehyde*) :

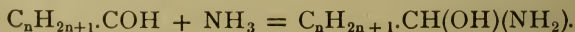


7. The aldehydes combine directly with the acid sulphites of the alkali metals, forming crystalline compounds, from which the aldehydes may be again obtained on treatment with a mineral acid or an alkaline carbonate :

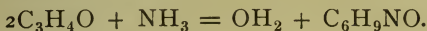


These compounds afford a ready means of purifying aldehydes.

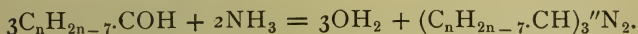
8. The aldehydes of the acetic or  $C_nH_{2n+1}.COH$  series combine directly with ammonia, forming crystalline compounds, the so-called *aldehyde-ammonias* :



The aldehydes of the acrylic or  $C_nH_{2n-1}.COH$  series appear to behave differently—thus acrolein yields the compound  $C_6H_9NO$  :

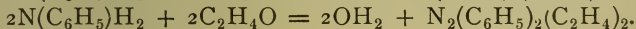
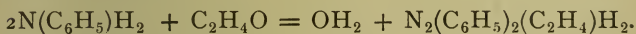


By the action of ammonia on the aldehydes of the benzoic and allied series, the whole of the oxygen of the aldehyde is at once eliminated in the form of water, and so-called *hydramides* are produced :



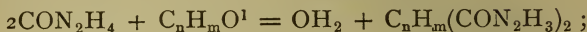
The aldehyde-ammonias are mostly resolved into the aldehyde and an ammoniac salt on treatment with acids ; on heating, either alone or with dehydrating agents, the oxygen they contain is partially or wholly removed in the form of water, and ammonia also split off, and a series of basic condensation-products, *oxaldines* and *aldines*, is formed.<sup>1</sup>

9. By the action of aniline on the aldehydes, numerous *phenylated-aldines* are produced, the oxygen of the aldehyde being eliminated in the form of water ; thus in the case of acetic aldehyde :

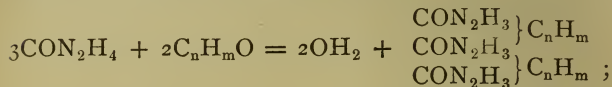


Considerable interest attaches to many of the products thus obtained. Thus Schiff has recently shown that on digesting normal butyric aldehyde with an alcoholic solution of ammonia, it is converted into *dibutyraldine*,  $C_8H_{17}NO = 2C_4H_8O + NH_3 - OH_2$  ; and that on dry distillation this product is converted into a substance of the same composition as *conine*,  $C_8H_{15}N$ , the poisonous alkaloid contained in hemlock. This artificial conine possesses almost all the properties of natural conine, with which, however, it appears to be isomeric and not identical, natural conine being probably a derivative of isobutyric aldehyde. Similarly, Baeyer has shown that by submitting acrolein-ammonia— $C_6H_9NO$ —to dry distillation, it is converted into *picolin*— $C_6H_7N$ —a basic substance formed by the destructive distillation of animal matters, &c.

The aldehydes behave similarly with urea : by their action on a concentrated aqueous or alcoholic solution of urea so-called *diureides* are produced, thus :

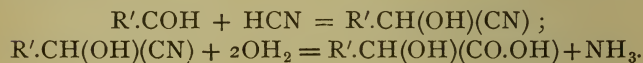


whilst by their action on dry urea *triureides* are formed :

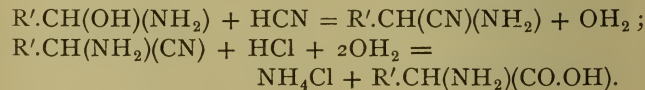


and similarly even still more complex compounds may be obtained. The ureides are readily resolved by the action of boiling water, or diluted acids, into the aldehydes and urea.

10. The aldehydes combine directly with hydrocyanic acid; on heating the compounds formed with dilute hydrochloric acid, oxy-acids containing one unit of carbon more than the aldehyde employed are produced (see *lactic acid*) :



Corresponding amido-acids are obtained on digesting the aldehyde-ammonias (p. 218) with hydrocyanic acid, and subsequently heating the product with dilute hydrochloric acid :



11. Many of the aldehydes also combine with such compounds as monochlorethane (ethylic chloride)— $\text{C}_2\text{H}_5\text{Cl}$ , acetic chloride— $\text{C}_2\text{H}_3\text{OCl}$ , acetic anhydride— $(\text{C}_2\text{H}_3\text{O})_2\text{O}$ , alcohol, hydrochloric acid, and water. All these additive compounds are highly unstable, however, and are readily resolved into their components.

This expression denotes generally an aldehyde derived from a monohydric alcohol.

$C_nH_{2n+1}.COH$  OR ACETIC SERIES OF ALDEHYDES.

The following members of the series are known<sup>1</sup> :—

|                                  |                           | B.-P.         |
|----------------------------------|---------------------------|---------------|
| Formic or methylic aldehyde      | $H.CO H$                  | gaseous.      |
| *Acetic or ethylic               | $CH_3.CO H$               | 22°           |
| *Propionic or propylic           | $C_2H_5.CO H$             | 48°·5         |
| *Butyric or tetrylic             | $C_3H_7^{\alpha}.CO H$    | 75°           |
| Isobutyric or isotetrylic        | $C_3H_7^{\beta}.CO H$     | 60°–62°       |
| *Valeric or pentylic             | $C_4H_9^{\alpha}.CO H$    | 102°          |
| †Isovaleric or isopentylic       | $C_4H_9^{\beta}.CO H$     | 93°           |
| †Caproic or hexylic              | $C_5H_{11}^{\beta}.CO H$  | 121°          |
| *Cenanthylic or heptylic         | $C_6H_{13}^{\alpha}.CO H$ | 152°          |
| Caprylic or octylic <sup>2</sup> | $C_8H_{16}O$              | 171°–178°     |
| Palmitic or hexdecylic           | $C_{16}H_{32}O$           | melts at 52°. |

FORMIC OR METHYLIC ALDEHYDE,  $CH_2O = HCOH$ .—

<sup>1</sup> Doubtless every alcohol  $R'.OH$  is convertible into a corresponding acid  $R'.CO(OH)$ —(see acids, preparation of, p. 242)—capable in turn of yielding a corresponding aldehyde  $R'.COH$ . The aldehydes derived from primary alcohols may be termed primary, those derived from secondary termed secondary, those derived from tertiary termed tertiary; and the aldehydes derived from isoprimary, isosecondary, or isotertiary alcohols termed isoprimary, &c. Thus:—

$C(C_nH_{2n+1})H_2.OH$  ;  $C(C_nH_{2n+1})_2H.OH$  ;  $C(C_nH_{2n+1})_3.OH$ .  
 Primary carbinol.                      Secondary carbinol.                      Tertiary carbinol.

$C(C_nH_{2n+1})H_2.CO H$  ;  $C(C_nH_{2n+1})_2H.CO H$  ;  $C(C_nH_{2n+1})_3.CO H$ .  
 Primary aldehyde.                      Secondary aldehyde.                      Tertiary aldehyde.

The aldehydes marked thus \* in the above list are normal primary aldehydes, being derived from normal primary alcohols; those marked † are isoprimary and are derived from the isoprimary alcohols of fermentation. Isobutyric aldehyde, obtained by oxidising isoprimary butylic alcohol, may be regarded as the first term of the series of normal secondary aldehydes of the acetic series. It will be noticed that the rise in boiling-point in the series of normal primary aldehydes corresponding to each addition of  $CH_2$  is about 26°.

<sup>2</sup> From castor-oil (see *ricinoleic acid*).

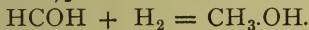
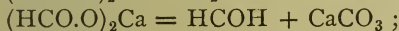
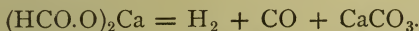
Until recently all attempts to prepare this aldehyde by the ordinary methods had proved unsuccessful, but Hofmann has shown that if certain precautions are observed it may be obtained by oxidation of methylic alcohol.

A current of air charged with vapour of the alcohol is directed upon an incandescent spiral of platinum wire suspended in a tubulated glass bottle, and afterwards passed through tubes surrounded by a refrigerating mixture. The heat generated by the oxidation of the alcohol is sufficient to keep the wire in a state of glow if the air-current be properly regulated. The liquid which condenses in the tubes is a solution of formic aldehyde in methylic alcohol which at once reduces an ammoniacal solution of argentic nitrate, the aldehyde being oxidised to formic acid. It is not possible, however, to isolate the aldehyde from this solution: if the alcohol be evaporated by exposure of the liquid over sulphuric acid *in vacuo*, a yellowish-white amorphous substance remains, which is a polymeride of formic aldehyde.

This polymeride probably has the composition  $C_3H_6O_3 = 3CH_2O$ , and is identical with the so-called *dioxymethylene*, obtained by Butlerow by treating methylene iodide (diiodomethane) with argentic oxide:  $xCH_2I_2 + xAg_2O = xCH_2O + 2xAgI$ . On heating, under reduced pressure (in Hofmann's vapour-density apparatus, p. 22), it is converted into the gaseous normal aldehyde,  $CH_2O$ , which, however, on cooling is slowly reconverted into the polymeride, so that it appears to have but an ephemeral existence. On passing sulphuretted hydrogen into the above-mentioned alcoholic solution, the aldehyde is converted into the corresponding *thialdehyde*,  $C_xH_{2x}S_x$  ( $x=3$ ), a white crystalline substance, melting at  $216^\circ$ ; the same compound is obtained by the action of nascent hydrogen on carbonic disulphide:  $xCS_2 + 2xH_2 = C_xH_{2x}S_x + xSH_2$ . By the action of ammonia on dioxymethylene (formic aldehyde) a crystalline compound (*hexmethylenamine*) of the formula  $C_6H_{12}N_4 = 2C_3H_6O_3 + 4NH_3 - 6OH_2$  is obtained. On boiling dioxymethylene with a solution of baric hydrate, it is converted into

*methylenitan* and formic acid. Methylenitan is said to have the composition  $C_7H_{14}O_6$ , but this does not appear to have been satisfactorily established; in many respects it closely resembles the natural sugars, and on this account a renewed investigation of the reaction is much to be desired.

The liquid product of the dry distillation of calcic formate  $[(HCO.O)_2Ca]$  contains a considerable proportion of methylic alcohol; it appears probable that formic aldehyde is first formed, but is converted by the action of hydrogen, simultaneously evolved, into methylic alcohol, thus:



According to recent researches of Baeyer, formic aldehyde is a body capable of entering into reaction with a very large number of compounds of various classes. In the case of the hydrocarbons of the aromatic series, the primary reaction appears always to be of the character indicated by the equation:



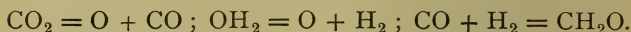
the product thus obtained, however, may, and indeed often does, in turn react with a further portion of the aldehyde in a similar manner. The phenols, resorcin, pyrogallol, and the oxy-acids, such as salicylic acid, gallic acid, &c., are also attacked by formic aldehyde: water is eliminated, and new complex compounds result.<sup>2</sup> Reactions of this kind, which

<sup>1</sup> If benzene be used, diphenylmethane,  $CH_2(C_6H_5)_2$ , is formed.

<sup>2</sup> To effect these changes Baeyer employs either a solution of the aldehyde in acetic acid prepared by heating methylene iodide ( $CH_2I_2$ ) with acetic acid and argentic acetate at  $100^\circ$  and subsequently digesting the portion of the product which passes over on distillation at  $130^\circ$ – $170^\circ$  with an equal weight of water in closed tubes at  $100^\circ$ , or *methylal*,  $CH_2(OCH_3)_2$  (p. 230). The acetic solution, or the methylal, is dissolved together with the substance to be acted upon in glacial



appear moreover to be specially characteristic of the aldehydes as a class,<sup>1</sup> claim the attention of the vegetable physiologist. There can be little doubt that formic aldehyde is one of the first substances generated in the plant from the carbonic anhydride and water which are absorbed and decomposed within the plant, apparently under the combined influence of the chlorophyl and sunlight: it may be supposed that carbonic anhydride is reduced to carbonic oxide, and water simultaneously resolved into its elements oxygen and hydrogen, and that the latter and carbonic oxide unite to produce formic aldehyde<sup>2</sup>:



ACETIC or ETHYLIC ALDEHYDE,  $\text{C}_2\text{H}_4\text{O} = \text{CH}_3\text{.COH}$ , commonly known as *aldehyde*, is the first product of the action of nearly every oxidising agent on ethylic alcohol; it

acetic acid, and concentrated sulphuric acid then cautiously added; the product is usually extracted from the mixture by shaking with ether. Mesitylene (p. 126) treated in this manner yields a crystalline hydrocarbon, *dimesitylmethane*— $\text{CH}_2(\text{C}_9\text{H}_{11})_2$ —which is formed with such readiness that the reaction may be employed as a means of detecting either formic aldehyde or mesitylene; thus dimesitylmethane is even obtained with the aid of a mixture of cold solutions of chromic anhydride and methylic alcohol in glacial acetic acid, proving that under these circumstances methylic alcohol is normally oxidised to formic aldehyde, although the latter cannot be isolated by ordinary means.

<sup>1</sup> All aldehydes which can be mixed with concentrated sulphuric acid without undergoing alteration appear to react in the manner indicated with aromatic hydrocarbons; but the various changes which take place rapidly on heating, or which are induced and hastened by the employment of dehydrating agents such as sulphuric acid, &c., doubtless can occur at ordinary temperatures, and without such extraneous aid, *i.e.* under conditions similar to those which obtain in plants, although necessarily in a slow and gradual manner.

<sup>2</sup> Recent experiments of Sir B. Brodie and the brothers Thénard tend to show that formic aldehyde is produced when a mixture of carbonic oxide and hydrogen gas is submitted to the action of the silent electric discharge.

is most conveniently prepared with the aid of a mixture of potassic dichromate solution and sulphuric acid.

The product is in all cases more or less contaminated with alcohol and acetic acid ; it is therefore allowed to remain for some hours in contact with about its own weight of calcic chloride and then distilled ; the distillate is mixed with thrice the volume of ether and saturated with ammonia gas, the crystalline aldehyde-ammonia which forms is collected, washed with ether, pressed between folds of bibulous paper, and decomposed by distillation with diluted sulphuric acid on the water bath ; finally the distillate is digested with calcic chloride and rectified.

Aldehyde is a colourless mobile liquid, possessing a peculiar characteristic ethereal, but suffocating odour ; it boils at  $22^{\circ}$ , and at  $0^{\circ}$  has the specific gravity  $\cdot 805^{\circ}$ . Aldehyde is soluble in all proportions in water and alcohol ; it is neutral to test paper, but gradually becomes acid on exposure to the air. All oxidising agents rapidly convert aldehyde into acetic acid ; on warming an aqueous solution to which argentic nitrate and a drop of ammonia has been added, a brilliant film of metallic silver is deposited on the inner surface of the vessel. On heating aldehyde with an aqueous or alcoholic solution of potassic hydrate, a brown resinous substance, the so-called aldehyde-resin, is produced ; similar products are obtained from all the homologous aldehydes of the acetic series. Aldehyde dropped upon molten potassic hydrate is converted into potassic acetate. On passing sulphuretted hydrogen into an aqueous solution of aldehyde, a heavy oil is thrown down, which is a compound of aldehyde with thialdehyde, and is resolved by treatment with acids into these two bodies. Thialdehyde crystallises in white needles having an alliaceous odour ; the determination of its vapour-density has shown that it has the composition  $C_6H_{12}S_3$ , so that it does not correspond to aldehyde  $C_2H_4O$ , but to the polymeride of aldehyde,  $C_6H_{12}O_3$ .

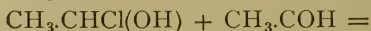
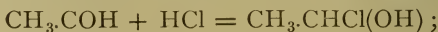
*Polymerides of Aldehyde.*—Pure aldehyde may be preserved unchanged in closed vessels, but on the addition of mere

traces of hydrochloric, sulphurous, or sulphuric acid, or of zincic chloride, &c., &c., it is noticed that the liquid soon becomes spontaneously heated, and to such a degree that it even enters into ebullition, the aldehyde being almost entirely converted into *paraldehyde*,  $C_6H_{12}O_3 = 3C_2H_4O$ . Paraldehyde is a clear colourless liquid at ordinary temperatures, boiling at  $124^\circ$ , but if cooled to below  $10^\circ$  it solidifies to a white crystalline mass ; on distillation with a small quantity of sulphuric acid it is reconverted into aldehyde.

A second polymeride, *metaldehyde*,  $C_{2x}H_{4x}O_x$ , is obtained if, on the addition of either of the above-mentioned substances, the aldehyde be carefully cooled by a refrigerating mixture ; after some time white crystalline needles of metaldehyde separate from the liquid. The relation of metaldehyde to aldehyde has not yet been ascertained ; it is reconverted into aldehyde on heating.

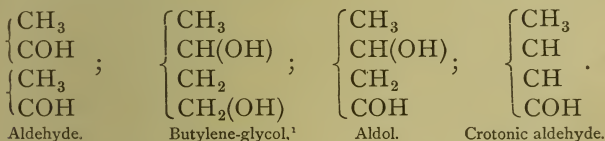
*Condensation Products of Aldehyde.*—1. The main product of the action of sodium amalgam upon an aqueous solution of aldehyde is ethylic alcohol, but if the solution be maintained slightly acid by repeated additions of hydrochloric acid, a small quantity of butylene-glycol ( $C_4H_{10}O_2$ ) is also produced :  $2C_2H_4O + H_2 = C_4H_{10}O_2$ .

2. If a mixture of aldehyde, water, and hydrochloric acid, which has stood about fourteen days, be neutralised with sodic carbonate, and shaken up with ether, the latter extracts a viscid colourless liquid of the composition  $C_4H_8O_2$ . The reaction which gives rise to the formation of *aldol*, as this product is termed, probably includes the phases :



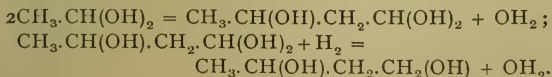
Aldol is the aldehyde of an oxybutyric acid ; it is converted into butylene-glycol by the action of nascent hydrogen, and into oxybutyric acid on oxidation by argentic oxide ; on distillation it is split up into water and crotonic aldehyde.

3. If pure aldehyde is heated with a very small quantity of zinc chloride and a few drops of water in closed vessels, during one to two days, at  $100^{\circ}$ , it is in a great measure converted into crotonic aldehyde,  $C_4H_6O = 2C_2H_4O - OH_2$ , a colourless mobile liquid boiling at  $104^{\circ}$ ; higher condensation products, of which little is known, are also formed simultaneously. Small quantities of numerous other substances (sulphuric and sulphurous acid, carbonic chloride, many salts, &c.) are capable of thus converting aldehyde into crotonic aldehyde; moreover, the change may be effected, although slowly, at ordinary atmospheric temperatures, and in presence of large quantities of water. The formation of crotonic aldehyde is probably preceded by that of aldol. The relation of aldehyde to butylene glycol, aldol, and crotonic aldehyde is indicated by the following formulæ :



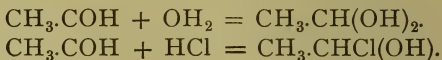
*Action of Chlorine on Aldehyde.*—The products of the action of chlorine vary greatly, according to the conditions of experiment. If aldehyde be introduced into a large flask filled with chlorine, violent reaction ensues, and acetic chloride is produced :  $CH_3.COH + Cl_2 = CH_3.COCl + HCl$ . The same result obtains on passing chlorine into a well-cooled solution of aldehyde in carbonic tetrachloride exposed to sunshine. In both cases a certain quantity of a compound of aldehyde and acetic chloride,  $C_2H_4O$ ,  $C_2H_3OCl = CH_3.CHCl(O.C_2H_3O)$ , is produced.

<sup>1</sup> Butylene-glycol is probably formed in the manner indicated by the following equations :

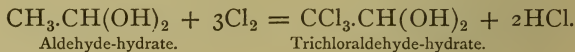


If, however, chlorine be passed into aldehyde, which at first is well cooled, but afterwards heated to  $100^{\circ}$ , until it ceases to be absorbed, the product consists of *trichlorocrotonic aldehyde*,  $C_4H_3Cl_3O$ . In this case, by the first action of the chlorine, hydrochloric acid is produced, whereby the aldehyde is converted into crotonic aldehyde, and by the continued action of chlorine the latter is transformed into trichlorocrotonic aldehyde.

If aldehyde be mixed with water, or a moderately dilute aqueous solution of hydrochloric acid, a considerable rise of temperature occurs, proving, it can scarcely be doubted, that chemical combination has taken place, thus :



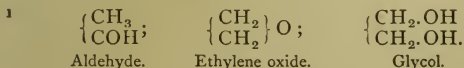
If either of these solutions, placed in a retort, and cooled to  $-10^{\circ}$ , be acted upon by chlorine, and after the action has continued some time at the low temperature, the mixture be gradually heated in the water-bath, and the current of chlorine still passed in, a considerable quantity of an oily liquid distils over, which is a mixture of the hydrates of di- and trichloraldehyde (chloral), thus :



TRICHLORALDEHYDE (*Chloral*),  $C_2HCl_3O = CCl_3.COH$ . The formation of chloral from alcohol and aldehyde has already been fully dwelt upon. Chloral is a colourless, heavy liquid (sp. gr. 1.5), which boils at  $94^{\circ}$ ; when kept it undergoes spontaneous modification, being converted into a white, insoluble, amorphous polymeride—so called *meta-chloral*, which is reconverted into chloral on distillation. On mixing chloral with water, much heat is evolved, and it is converted into *chloral-hydrate*,  $CCl_3.CH(OH)_2$ , a white crystalline substance which distils unchanged, but is

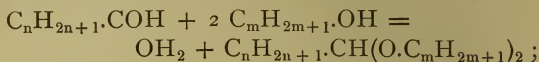
broken up into its generators when heated a few degrees above its boiling-point ( $95^{\circ}$ ). Chloral also combines with ethylic alcohol, and its homologues, and the corresponding mercaptans to form crystalline compounds, such as  $\text{CCl}_3\cdot\text{CH}(\text{OH})(\text{OC}_2\text{H}_5)$  and  $\text{CCl}_3\cdot\text{CH}(\text{OH})(\text{SC}_2\text{H}_5)$ ; all these when heated a few degrees above their boiling-points are resolved into their generators. The compounds of chloral with water and the alcohols are also decomposed on treatment with concentrated sulphuric acid, chloral being liberated. On oxidation chloral is converted into trichloroacetic acid,  $\text{CCl}_3\cdot\text{CO}(\text{OH})$ . Chloral is readily decomposed by alkalis, trichloromethane (chloroform) and a formate being produced:  $\text{CCl}_3\cdot\text{COH} + \text{KHO} = \text{CCl}_3\text{H} + \text{HCO}(\text{OK})$ . Chloral-hydrate introduced under the skin, or administered internally, is similarly resolved into chloroform and formic acid; the physiological action of chloroform thus generated within the system, as it were, is to produce deep sleep, but not insensibility to pain as when inhaled. By the action of nascent hydrogen chloral is reduced to aldehyde. Chlorine is without action on chloral, even in presence of antimonious chloride; phosphorus pentachloride converts chloral into pentachlorethane,  $\text{C}_2\text{HCl}_5$ . In presence of concentrated sulphuric acid chloral readily acts upon benzene and the homologous hydrocarbons; thus:  $2\text{C}_6\text{H}_6 + \text{C}_2\text{HCl}_3\text{O} = \text{OH}_2 + \text{C}_2\text{HCl}_3(\text{C}_6\text{H}_5)_2$ .

*Acetals*.—The aldehydes of the acetic series are isomeric with the ethers derived from the glycols containing the same number of units of carbon; thus acetic aldehyde (B.-P.  $22^{\circ}$ ) is isomeric with ethylene oxide (B.-P.  $13^{\circ}.5$ ), the ether of glycol.<sup>1</sup> Similarly, the mixed ethers of the form  $\text{C}_n\text{H}_{2n}(\text{O}\cdot\text{C}_m\text{H}_{2m+1})_2$  derived from the glycols (p. 208) are isomeric with the acetals, which are a class of compounds

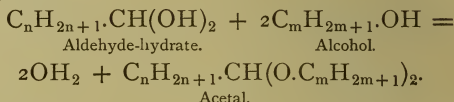




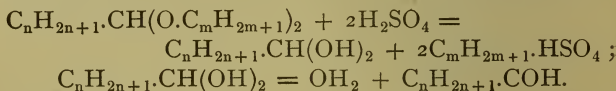
formed by the union of the aldehydes of the acetic series with the alcohols of the ethylic series with simultaneous elimination of the elements of water ; thus :



or more probably :

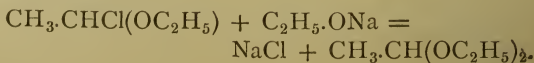


The acetals are decomposed by concentrated sulphuric acid, probably in the manner indicated by the equations .



*Methylal*,  $\text{CH}_2(\text{OCH}_3)_2$ , the first term of the series, is obtained by distilling a mixture of methylic alcohol, manganese peroxide, and sulphuric acid : the alcohol is doubtless in part oxidised to formic aldehyde, which at the moment of formation reacts on a further portion of the alcohol, producing methylal. It is a colourless liquid boiling at  $42^\circ$ .

*Acetal*,  $\text{CH}_3\cdot\text{CH}(\text{OC}_2\text{H}_5)_2$ , isomeric with the mixed ether  $\text{C}_2\text{H}_4(\text{OC}_2\text{H}_5)_2$  derived from glycol, is similarly prepared by partially oxidising ethylic alcohol. It is also one of the main products at first formed by the action of chlorine on alcohol. When gaseous hydrochloric acid is passed into a solution of aldehyde in anhydrous alcohol, the product of their union,  $\text{CH}_3\cdot\text{CH}(\text{OH})(\text{OC}_2\text{H}_5)$ , which may be supposed to be present, is converted into the compound  $\text{CH}_3\cdot\text{CHCl}(\text{OC}_2\text{H}_5)$ , which is identical with the first product of the action of chlorine on ethylic ether ; on heating this compound with sodic ethylate, acetal is formed, thus :



Acetal is a colourless liquid of agreeable ethereal odour, boiling at  $104^{\circ}$ ; the isomeric ether from glycol boils at  $123^{\circ}.5$ .

Comparatively little is known of the higher homologues of acetic aldehyde.

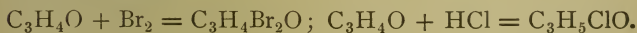
### $C_nH_{2n-1}.COH$ OR ACRYLIC SERIES OF ALDEHYDES.

Two aldehydes of this series are known, namely :—

|                              |           | B.-P.           |
|------------------------------|-----------|-----------------|
| Acrylic aldehyde or acrolein | $C_3H_4O$ | $52^{\circ}.5$  |
| Crotonic aldehyde            | $C_4H_6O$ | $104^{\circ}.5$ |

ACRYLIC ALDEHYDE (*Acrolein*),  $C_3H_4O = CH_2.CH.CO H$ , is formed on oxidation of allylic alcohol by chromic acid, but the greater portion is at once further oxidised; it is best prepared by distilling glycerin with a dehydrating agent, such as phosphoric anhydride, or hydric potassic sulphate:  $C_3H_8O_3 = 2OH_2 + C_3H_4O$ . Acrolein is a constant product of the destructive distillation of all fats containing glycerides.

Acrolein is a colourless mobile liquid; the vapour has an indescribably irritating action on the eyes and nose, a few drops sufficing to render the atmosphere of a large room absolutely unbearable. Acrolein is readily oxidised by argentic oxide to acrylic acid,  $C_3H_4O_2$ ; more powerful oxidising agents, such as chromic acid, convert it into formic acid, carbonic anhydride, and water. Nascent hydrogen (sodium amalgam and water) reduces acrolein to allylic alcohol. It combines with chlorine, bromine, the haloid acids, &c., thus:



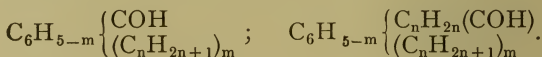
### $C_nH_{2n-5}.COH$ SERIES OF ALDEHYDES.

Aldehydes of the  $C_nH_{2n-3}.COH$  and  $C_nH_{2n-5}.COH$  series have not hitherto been obtained, but two isomeric bodies, *furfural* and *fucusal*, are known, which appear to be monooxy-derivatives of an aldehyde ( $C_5H_4O$ ) of the latter series.

FURFUROL, FUCUSOL,  $C_5H_4O_2 = C_4H_2(OH).COH$ .—The former is obtained by carefully distilling wheat bran with diluted sulphuric acid; the latter by similar treatment of several varieties of *fucus*. When freshly prepared both are colourless oils, but rapidly become yellow; furfurol boils at  $162^\circ$ , fucusol at  $171^\circ$ – $172^\circ$ ; on oxidation by argentic oxide they are respectively converted into  $\alpha$ - and  $\beta$ -pyromucic acid. Furfurol combines with hydric sodic sulphite; by the action of sulphuretted hydrogen it is converted into *thiofurfurol*,  $C_5H_4OS$ ; fucusol similarly treated yields *thiofucusol*. By the action of ammonia furfurol and fucusol are converted into isomeric crystalline compounds  $[3C_5H_3(OH)O + 2NH_3 = 3OH_2 + (C_5H_3.OH)_3N_2]$ , *furfuramide* and *fucusamide*: these are perfectly neutral substances, but on boiling with potassic hydrate solution they undergo a remarkable change and are converted into the isomeric, powerfully basic compounds *furfurine* and *fucusine*, each of which furnishes well-crystallised salts, such as  $C_{15}H_{12}N_2O_3.HCl$ , &c.

#### $C_nH_{2n-7}.COH$ OR BENZOIC SERIES OF ALDEHYDES.

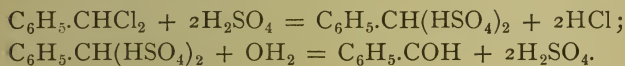
The series includes two classes of metameric aldehydes, corresponding to the two classes of monohydric alcohols derived from the aromatic hydrocarbons, and represented respectively by the general expressions:



The following members of the series are known:—

|                  |   |                      | B.-P.         |
|------------------|---|----------------------|---------------|
| Benzoic aldehyde | . | $C_6H_5.COH$         | . $180^\circ$ |
| Paratoluic       | „ | $C_6H_4(CH_3).COH$   | . $204^\circ$ |
| Alpha-toluic     | „ | $C_6H_5.CH_2(COH)$   | . —           |
| Cumic            | „ | $C_6H_4(C_3H_7).COH$ | . $236^\circ$ |
| Sycocerylic      | „ | $C_{18}H_{28}O$      | . —           |

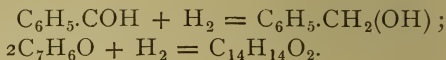
BENZOIC ALDEHYDE (*Bitter-Almond Oil*, *Benzaldehyde*),  $\text{C}_7\text{H}_6\text{O} = \text{C}_6\text{H}_5\cdot\text{COH}$ .—This aldehyde may be produced by oxidation of benzylic alcohol,  $\text{C}_6\text{H}_5\cdot\text{CH}_2(\text{OH})$ ; by distillation of an intimate mixture of calcic benzoate and formate; by passing a mixture of hydrogen gas and benzoic chloride vapour over heated finely-divided palladium:  $\text{C}_6\text{H}_5\cdot\text{COCl} + \text{H}_2 = \text{C}_6\text{H}_5\cdot\text{COH} + \text{HCl}$ ; and by treating benzylene chloride with concentrated sulphuric acid, and subsequently distilling the product with water:



Benzoic aldehyde is usually prepared by digesting bitter almond meal with water during five to six hours at  $30^\circ$ – $40^\circ$  (whereby the amygdalin becomes converted under the influence of the synaptase present into benzoic aldehyde, hydrocyanic acid, and glucose), and subsequently distilling the liquid. Small quantities of benzoic aldehyde are obtained, together with numerous other products, by the oxidation of albumin, fibrin, casein, and gelatin.

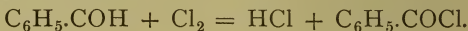
Benzoic aldehyde is a colourless mobile liquid of high refractive power and agreeable aromatic odour; sp. gr. 1.063 at  $0^\circ$ ; it is soluble in about 30 parts of cold water, and dissolves in all proportions in alcohol and ether. On exposure to the air, benzoic aldehyde rapidly absorbs oxygen and is converted into crystalline benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{CO}(\text{OH})$ ; by very concentrated nitric acid it is converted into nitrobenzoic aldehyde,  $\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{COH}$ ; by a less concentrated acid it is oxidised to benzoic acid. It forms crystalline compounds with the acid sulphites of the alkali metals, such as  $\text{C}_7\text{H}_6\text{O}\cdot\text{NaHSO}_3$ , &c. By the action of fused potassic hydrate, benzoic aldehyde is converted into potassic benzoate, and hydrogen is evolved; with an alcoholic solution of potassic hydrate it yields benzylic alcohol and potassic benzoate. By the action of sodium amalgam on a solution of benzoic aldehyde in aqueous alcohol, benzylic alcohol and two

isomeric crystalline compounds ( $\alpha$ - and  $\beta$ -hydrobenzoin<sup>1</sup>) are produced, thus :



The action of ammonia on benzoic aldehyde gives rise to the formation of *hydrobenzamide*:  $3\text{C}_7\text{H}_6\text{O} + 2\text{NH}_3 = 3\text{OH}_2 + (\text{C}_7\text{H}_6)_3\text{N}_2$ , a white crystalline neutral body, which is converted into an isomeric basic compound, *amarine*, on boiling with potassic hydrate solution.

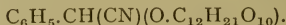
By the action of chlorine, benzoic aldehyde is converted into benzoic chloride :



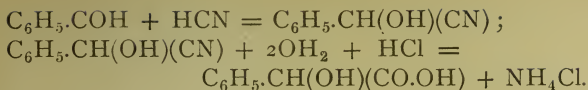
Benzoic aldehyde combines with hydrocyanic acid forming *hydrocyanbenzaldehyde*, which yields *mandelic acid*<sup>2</sup> on digestion with an aqueous solution of hydrochloric acid :

<sup>1</sup>  $\alpha$ -Hydrobenzoin crystallises in large glistening anhydrous plates and melts at  $132^\circ\cdot 5$  ;  $\beta$ - (iso-) hydrobenzoin crystallises in thin glistening four-sided prisms, which contain water of crystallisation—in the anhydrous state it melts at  $119^\circ\cdot 5$  ; it is more soluble in alcohol than  $\alpha$ -hydrobenzoin. A relatively larger quantity of  $\beta$ -hydrobenzoin is formed by the action of sodium amalgam on a heated mixture of benzoic aldehyde and water, and a relatively larger quantity of  $\alpha$ -hydrobenzoin by acting upon an alcoholic solution of the aldehyde at ordinary temperatures, the amount obtained increasing with the concentration of the alcohol.  $\alpha$ -Hydrobenzoin was originally obtained by Zinin by the action of zinc and hydrochloric acid on benzoic aldehyde.  $\alpha$ - and  $\beta$ -hydrobenzoin yield chlorinated derivatives,  $\text{C}_{14}\text{H}_{12}\text{Cl}_2$ , on treatment with  $\text{PCl}_5$ , which are converted into tolane,  $\text{C}_{14}\text{H}_{10}$ , by the action of an alcoholic solution of potassic hydrate.

<sup>2</sup> Mandelic acid is also obtained by boiling amygdalin from bitter almonds with an aqueous solution of baric hydrate, until ammonia ceases to be evolved. Amygdalin is a glucoside of hydrocyanbenzaldehyde, which may be represented by the formula

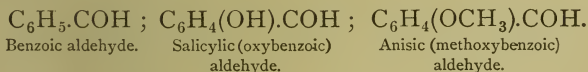


The decomposition which amygdalin undergoes under the influence of synaptase may be explained as follows : it is in the first place resolved



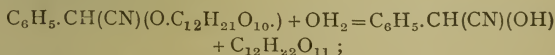
CUMIC ALDEHYDE,  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_7)\cdot\text{COH}$ , exists together with  $\alpha$ -cymene in the essential oil of cumin, and in that of water-hemlock (*Cicuta virosa*). It is separated from cymene either by fractional distillation, or by agitating the oil with a moderately concentrated aqueous solution of hydric sodic sulphite, which forms a crystalline compound with the aldehyde, which may be separated, and the aldehyde liberated by potassic hydrate. Cumic aldehyde closely resembles benzoic acid in all its reactions.

SALICYLIC ALDEHYDE ; ANISIC ALDEHYDE.—These two aldehydes, which are closely related to benzoic aldehyde, may be conveniently described here. The relation which they bear to benzoic aldehyde will be evident on comparing their formulæ :



*Salicylic Aldehyde* (*Salicylol*) exists ready formed in the flowers of meadow-sweet (*Spiræa ulmaria*), and may be obtained, together with a terpene, by distilling them with water. It is produced by oxidising the corresponding alcohol, saligenin,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2(\text{OH})$ , or *salicin*,  $\text{C}_6\text{H}_4(\text{OH})\cdot\text{CH}_2(\text{O}\cdot\text{C}_6\text{H}_{11}\text{O}_5)$ . Salicylol is a mobile, colourless fragrant oil, slightly soluble in water, boiling at  $196^\circ.5$  ;

by assumption of the elements of water into hydrocyanbenzaldehyde and a sugar (saccharose ?) :



the latter is in turn converted into glucose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{OH}_2 = 2\text{C}_6\text{H}_{12}\text{O}_6$ ), whilst the hydrocyanbenzaldehyde, which is a highly unstable substance, is resolved into hydrocyanic acid and benzoic aldehyde.



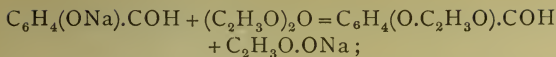
it is converted by oxidation into salicylic acid, by nascent hydrogen into saligenin, and by ammonia into *hydro-salicylamide* (oxyhydrobenzanide),  $(C_7H_5.OH)_3N_2$ . Chlorine, bromine, and concentrated nitric acid act readily upon salicyl, forming *chlorosalicyl*,  $C_6H_3Cl(OH).COH$ , *bromosalicyl*,  $C_6H_3Br(OH).COH$ , and *nitrosalicyl*,  $C_6H_3(NO_2)(OH).COH$ . Salicyl and all its substitution-derivatives unite with the acid sulphites of the alkali metals, forming crystalline compounds.

Salicyl dissolves in solutions of caustic alkalies, and even decomposes alkaline carbonates, producing crystalline metallic derivatives, such as *sodium-salicyl*,  $C_6H_4(ONa).COH$ , &c. On treating sodium-salicyl with methylic and ethylic iodide, methyl- and ethyl-salicyl,  $C_6H_4(OCH_3).COH$ ,  $C_6H_4(OC_2H_5).COH$ , are produced. Salicyl unites with acetic anhydride, forming a crystalline compound,  $C_{11}H_{12}O_5 = C_6H_4(OH).CH(OC_2H_3O)_2$ .

*Coumarin*.—By an interesting series of reactions Perkin has recently succeeded in converting salicyl into *coumarin*, the odoriferous principle of the Tonka bean,<sup>1</sup> in which it may often be seen forming minute colourless crystals under the skin of the seed and between the cotyledons. The following is the mode of synthesis employed by Perkin :—

Sodium-salicyl is added to acetic anhydride, in which it dissolves with considerable evolution of heat, the mixture is boiled for a few minutes and then poured into water, when an oily liquid separates while sodic acetate passes into solution; on distilling this oil, after small quantities of salicyl and acetic anhydride have passed over, the thermometer rises rapidly to  $290^\circ$ , at which temperature the remaining product, consisting of almost pure coumarin, distils and solidifies to a crystalline mass on cooling. The first change appears to consist in the formation of acetosalicyl and sodic acetate :

<sup>1</sup> Coumarin also exists in other plants: in *Melilotus officinalis*, combined with melilotic acid; in *Asperula odorata*; and in sweet vernal-grass (*Anthoxanthum odoratum*).



the second in the resolution of acetosalicyl into coumarin and water :



Perkin has shown that the final change is dependent on the presence of sodic acetate, no trace of coumarin being obtained on distilling acetosalicyl, or a mixture of acetosalicyl and acetic anhydride, although it is formed on heating a mixture of acetosalicyl, acetic anhydride, and sodic acetate to the boiling-point ; it is difficult, however, to understand what is the nature of the influence exerted by this salt.

Coumarin crystallises in slender colourless needles, which melt at about  $67^\circ$  and boil at  $290^\circ$ - $291^\circ$  ; it has no longer the properties of an aldehyde. On boiling with a concentrated aqueous solution of potassic hydrate, coumarin is converted into potassic coumarate,  $\text{C}_9\text{H}_7\text{KO}_3$  ; when fused with potassic hydrate it yields potassic salicylate and acetate.

*Anisic Aldehyde*,  $\text{C}_8\text{H}_8\text{O}_2 = \text{C}_6\text{H}_4(\text{OCH}_3).\text{COH}$ .—This aldehyde is formed, together with anisic acid, on oxidation of anisic alcohol, or of anise-oil<sup>1</sup> ; it is an oily liquid of fragrant odour, boiling at  $247^\circ$ . Anisic aldehyde is isomeric with methyl-salicyl (methyl-orthoxybenzoic aldehyde), being the methyl-derivative of paroxybenzoic aldehyde ; it closely resembles benzoic and salicylic aldehydes in its behaviour with reagents.

<sup>1</sup> Anise-oil is a solution of a solid substance—*anise-camphor* or *anethol*—in a fluid oil, which is probably a terpene. Recent experiments of Ladenburg show that anethol has the composition expressed by the formula  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_5).\text{OCH}_3$ , and that it may be converted by the action of potassic hydrate into the corresponding phenol—*anol* or *allylphenol*,  $\text{C}_6\text{H}_4(\text{C}_3\text{H}_5).\text{OH}$  ; anethol thus bears the same relation to anol that anisol,  $\text{C}_6\text{H}_5.\text{OCH}_3$ , bears to phenol. The reaction which occurs on oxidation of anethol to anisic aldehyde is represented by the equation :



$$C_nH_{2n-9}.COH$$
 SERIES OF ALDEHYDES.

CINNAMIC ALDEHYDE,  $C_9H_8O = CH(C_6H_5):CH.CO H$ , is the essential constituent of oil of cinnamon or oil of cassia ; it is a colourless oil, which rapidly absorbs oxygen on exposure to moist air, and is converted into cinnamic acid,  $C_9H_8O_2$ . In contact with ammonia, cinnamic aldehyde is converted into cinnhydramide— $(C_9H_8)_3N_2$  ; it forms crystalline compounds with the acid sulphites of the alkali metals.

*Aldehydes derived from Dihydric Alcohols.*

Only two such aldehydes are known, namely :

Oxalic aldehyde or glyoxal,  $C_2H_2O_2 = (COH)_2$

Terephthalic aldehyde,  $C_8H_6O_2 = C_6H_4(COH)_2$ .

*Glyoxal* bears the same relation to glycol and to oxalic acid that acetic aldehyde bears to ethylic alcohol, and to acetic acid, thus :

$CH_3.CH_2(OH)$  ;  $CH_3.CO H$  ;  $CH_3.CO(OH)$ .

Ethylic alcohol.

Acetic aldehyde.

Acetic acid.

$CH_2(OH).CH_2(OH)$  ;  $COH.CO H$  ;  $CO(OH).CO(OH)$ .

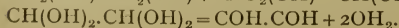
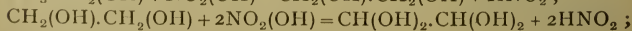
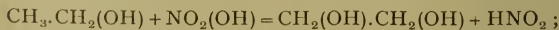
Glycol.

Glyoxal.

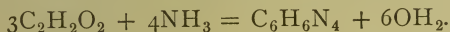
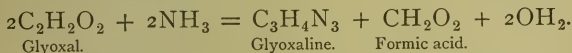
Oxalic acid.

Glyoxal was first obtained by Debus by oxidising alcohol with nitric acid ; oxalic acid and various other products are formed simultaneously.<sup>1</sup> It is a transparent amorphous deliquescent substance, very soluble in water, alcohol and ether ; it immediately reduces an ammoniacal solution of argentic nitrate, and is readily oxidised even by very dilute nitric acid to *glyoxalic acid*,  $COH.CO(OH)$ , and oxalic acid. Glyoxal combines with gaseous ammonia, and

<sup>1</sup> The formation of glyoxal is doubtless the result of a series of changes, which perhaps occur as traced by the following equations :



with the acid sulphites of the alkali metals; thus it unites with hydric sodic sulphite to form a crystalline compound— $\text{C}_2\text{H}_2\text{O}_2(\text{HNaSO}_3)_2 + \text{OH}_2$ ; it also combines with hydrocyanic acid (see *racemic acid*). On digesting glyoxal with strong aqueous ammonia, two crystalline bases, *glyoxaline* and *glycosine*, are produced, thus :



The supposed *phthalic aldehyde*, obtained by the action of nascent hydrogen on phthalic chloride,  $\text{C}_6\text{H}_4(\text{COCl})_2$  (the product of the action of  $\text{PCl}_5$  on phthalic acid), has recently been discovered to have the formula  $\text{C}_6\text{H}_4 \left\{ \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \right\} \text{O}$ .

## CHAPTER IX.

### ACIDS.

THE simplest and most probable interpretation of the reactions which occur on conversion of the primary alcohols into the corresponding acids by oxidation is, as already stated, afforded by the assumption that the  $\text{CH}_2\text{OH}$  group has undergone conversion into the  $\text{CO.OH}$  or carboxyl group; and a consideration of the other methods employed in the formation of acids, and of their behaviour with various reagents, has also led to the representation of these compounds, with few exceptions, by rational formulæ containing the expression  $\text{CO.OH}$ .

One of the most characteristic properties of the acids is that of forming metallic derivatives (*metallic salts*) when acted upon by *metallic carbonates*, the change consisting in all cases in the removal of hydrogen, and its replacement by the equivalent amount of the metal. It is found on careful

study of the behaviour of the acids under various circumstances that the number of units of hydrogen thus replaceable, in other words *the basicity of an acid*, is in direct relation to the number of times the expression  $\text{CO.OH}$  is contained in its rational formula: *an acid containing  $n$  carboxyl groups being  $n$ -basic*.

A large number of series of acids are known, which may be regarded as derived from the various series of isologous hydrocarbons by the replacement of one or more units of hydrogen by the carboxyl group a corresponding number of times. The following are the most important series of acids hitherto examined :—

#### Monobasic Acids.

Acetic or  $\text{C}_n\text{H}_{2n+1}\text{CO(OH)}$  series, derived from the  $\text{C}_n\text{H}_{2n+2}$  hydrocarbons

Acrylic or  $\text{C}_n\text{H}_{2n-1}\text{CO(OH)}$  series, derived from the  $\text{C}_n\text{H}_{2n}$  hydrocarbons

Sorbic or  $\text{C}_n\text{H}_{2n-3}\text{CO(OH)}$  series, derived from the  $\text{C}_n\text{H}_{2n-2}$  hydrocarbons

Benzoic or  $\text{C}_n\text{H}_{2n-7}\text{CO(OH)}$  series, derived from the  $\text{C}_n\text{H}_{2n-6}$  hydrocarbons

Cinnamic or  $\text{C}_n\text{H}_{2n-9}\text{CO(OH)}$  series, derived from the  $\text{C}_n\text{H}_{2n-8}$  hydrocarbons

Naphtoic or  $\text{C}_n\text{H}_{2n-13}\text{CO(OH)}$  series, derived from the  $\text{C}_n\text{H}_{2n-12}$  hydrocarbons

#### Dibasic Acids.

Succinic or  $\text{C}_n\text{H}_{2n}(\text{CO.OH})_2$  series, derived from the  $\text{C}_n\text{H}_{2n+2}$  hydrocarbons

Fumaric or  $\text{C}_n\text{H}_{2n-2}(\text{CO.OH})_2$  series, derived from the  $\text{C}_n\text{H}_{2n}$  hydrocarbons

Phthalic or  $\text{C}_n\text{H}_{2n-8}(\text{CO.OH})_2$  series, derived from the  $\text{C}_n\text{H}_{2n-6}$  hydrocarbons

#### Tribasic Acids.

Tricarballic or  $\text{C}_n\text{H}_{2n-1}(\text{CO.OH})_3$  series, derived from the  $\text{C}_n\text{H}_{2n+2}$  hydrocarbons

Mesitic or  $\text{C}_n\text{H}_{2n-9}(\text{CO.OH})_3$  series, derived from the  $\text{C}_n\text{H}_{2n-6}$  hydrocarbons

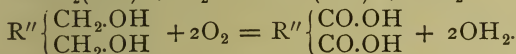
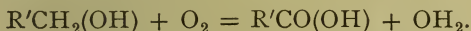
Closely related to one or other of these series are a variety of secondary series derived from them, such as the

Lactic or  $C_nH_{2n}(OH).CO(OH)$  series, derived from the acetic series  
 Malic or  $C_nH_{2n-1}(OH)(CO.OH)_2$  „ „ „ succinic „  
 Tartaric or  $C_nH_{2n-2}(OH)_2(CO.OH)_2$  „ „ „ succinic „  
 Salicylic or  $C_nH_{2n-8}(OH).CO(OH)$  „ „ „ benzoic „

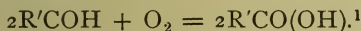
Acids of higher basicity, single terms of other series, and a large number of acids, mostly derived from plants, of which the genetic relations to the hydrocarbons have not yet been established, are also known.

*Preparation.*—Acids of the primary series above mentioned are produced by the following general methods:—

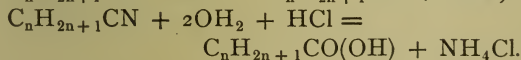
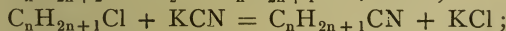
1. By oxidation of the corresponding primary alcohols :



2. By oxidation of the corresponding aldehydes :



3. From the hydrocarbons, which are first converted into haloid derivatives, these into the corresponding cyanides, and the cyanides decomposed by heating with water and a mineral acid or an alkali, thus :

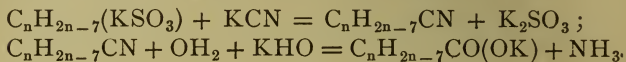


The haloid substitution-derivatives obtained from the hydrocarbons of the aromatic series and isologous series containing proportionately less hydrogen, by the action of chlorine

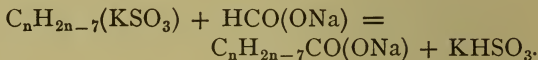
<sup>1</sup> Perhaps :  $RCOH + O + OH_2 = R'.CO(OH) + OH_2$  ; i.e. the reaction is one of double decomposition, H being replaced by OH, and does not consist in the mere addition of oxygen.



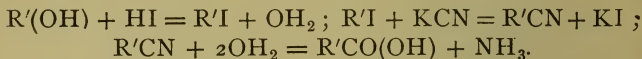
in the cold, are not convertible into cyanides by double decomposition with potassic cyanide. The corresponding cyanides may be obtained, however, by distilling the potassic salts of the sulphonic acids, obtained by the action of sulphuric acid on the hydrocarbons, with potassic cyanide :



The hydrocarbons of these series may also in many cases be directly converted into the corresponding acids by fusing the potassic salts of the sulphonic acids derived from them with sodic formate :



4. From the alcohols. The alcohol is submitted to the action of hydrobromic or hydriodic acid, the resulting bromide or iodide is converted into a cyanide by digestion with potassic cyanide, and the latter decomposed by heating with water and a mineral acid or an alkali :



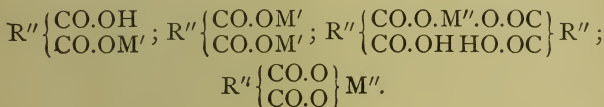
Obviously the acid obtained by the application of methods 3 and 4 always contains one unit of carbon more than the hydrocarbon or alcohol employed.

*General Properties.*—The acids of the various primary series exhibit an analogous behaviour under the influence of a large number of reagents.

*Metallic Salts.*—All the acids furnish metallic derivatives or *salts* when acted upon by the metallic carbonates, hydrates, or oxides. The composition of the *normal salts* containing monad metals derived from the monobasic acids is indicated by the general expression,  $\text{R}'\text{CO}(\text{OM}')$ , but, in addition to these, certain of the acids, notably those of the acetic series, furnish so-called *acid salts* of the composition indicated by

the formula  $R'CO(OM'), R'CO(OH)$ ; the composition of their normal salts containing polyad metals is indicated by the formulæ  $(R'CO_2)_2M'', (R'CO_2)_3M''', \&c.$ ; the monobasic acids also furnish a number of basic salts with polyad metals (see *acetic acid*).

Two series of salts, acid and normal, are obtained from the dibasic acids, according as one half or the whole of the replaceable hydrogen is replaced; the nature of the salts will be evident on inspection of the following formulæ:



In short, in every polybasic acid the  $n$  units of replaceable hydrogen may be replaced unit by unit. The metallic salts of the organic acids are at once decomposed by most mineral acids and the organic acid set free.

*Ethereal Salts.*—The ethereal salts, or compound ethers, as they are commonly termed, are the products of the action of the alcohols upon the acids; they bear precisely the same relation to the metallic salts that the alcohols bear to the metallic hydrates, thus:



A great variety of these compounds may be produced, inasmuch as the acids, both mineral and organic, of all degrees of basicity may be converted into ethereal salts derived not only from monohydric, but also from polyhydric alcohols, just as metallic salts may be obtained containing metals of varying degrees of equivalency.

Incidentally frequent mention has been made of various ethereal salts in the foregoing pages: for example, of the acid ethereal salts formed by the action of sulphuric acid on the alcohols; of the nitrins formed by the action of nitric acid on glycerin, mannite, cellulose, &c. Special names are

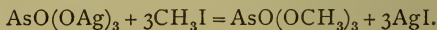
often applied to various sets of ethereal salts : thus the glyceric salts formed from glycerin and acetic, oleic, palmitic, and stearic acid, are termed respectively acetins, oleins, palmitins, and stearins.

Acid and normal ethereal salts of mineral and organic acids, corresponding to the acid and normal metallic salts, may be produced by the following general methods :—

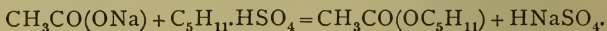
1. By the action of the alcohols on the acids : this method is more especially available for the preparation of ethereal salts of sulphuric and nitric acid.

2. By the action of the acid chlorides or anhydrides on the alcohols ; thus acetic chloride and ethylic alcohol yield ethylic acetate<sup>1</sup>:  $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\cdot\text{OH} = \text{CH}_3\text{CO}(\text{OC}_2\text{H}_5) + \text{HCl}$  ; and similarly, phosphoric chloride and ethylic alcohol yield ethylic phosphate :  $\text{POCl}_3 + 3\text{C}_2\text{H}_5\cdot\text{OH} = \text{PO}(\text{OC}_2\text{H}_5)_3 + 3\text{HCl}$ .

3. By the action of mono-haloid hydrocarbon derivatives on the argentic, potassic, or sodic salts of the acids : for example, methylic arsenate is obtained by the action of methylic iodide on argentic arsenate:



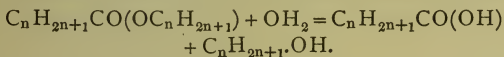
4. By the action of the acid ethereal salts of sulphuric acid on the potassic or sodic salts of the acids ; thus, hydric amylic sulphate and sodic acetate yield amylic acetate on distillation :



The majority of the ethereal salts are stable compounds and can be distilled unchanged ; on heating with water, or a solution of potassic hydrate, they are more or less readily resolved into

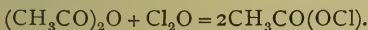
<sup>1</sup> The method usually adopted in the preparation of the ethereal salts of organic acids is a modification of this method, and consists in saturating a solution of the acid in the alcohol with gaseous hydrochloric acid ; apparently the acid is converted into water and the acid chloride, which at the moment of formation reacts upon the alcohol. It is impossible, however, in this way to convert the whole of the acid taken into the ethereal salt, since after a time the water produced is in such proportion that the acid chloride is converted as rapidly as it is formed into the acid and hydrochloric acid, and ceases to act upon the alcohol.

the acid, or potassic salt of the acid, and the alcohol from which they are derived ; the ethereal salts derived from the acids of the acetic series and the alcohols of the ethylic series, for example, are acted upon in the manner represented by the equation :

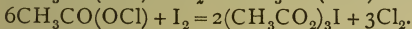
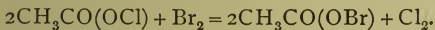


*Haloid Salts.*—These are formed from the metallic salts by the replacement of the metal by chlorine, bromine, or iodine. The haloid salts of acetic acid have chiefly been studied, but the homologous acids, and acids of other series, appear to be capable of furnishing similar derivatives.

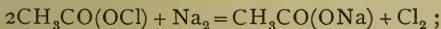
Chlorine acetate<sup>1</sup> is produced by the action of acetic anhydride on hypochlorous anhydride :



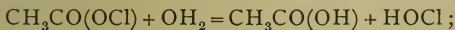
It is converted into the bromine salt by the action of bromine, and into the iodine salt by the action of iodine ; thus :



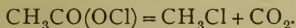
The iodine salt is obviously comparable with the metallic salts containing triad metals, iodine acetate being the analogue of bismuthic acetate,  $(\text{CH}_3\text{CO}_2)_3\text{Bi}$ , for example. These haloid salts are eminently unstable compounds ; thus chlorine acetate is at once decomposed in the cold by metals such as zinc, mercury, copper, or sodium, with evolution of chlorine and formation of the corresponding metallic salt, e.g. :



it is converted by water into acetic and hypochlorous acids :



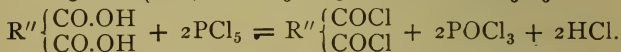
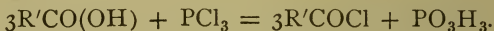
on heating it is decomposed at a temperature below  $100^\circ$  with explosion :



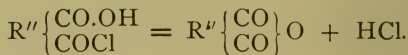
<sup>1</sup> Chlorine acetate is a yellow liquid ; iodine acetate a crystalline solid.

*Haloid Substitution-derivatives.*—By the action of chlorine or bromine on the acids of the acetic, benzoic, naphtoic, succinic, and phthalic series, one or more units of hydrogen are removed and replaced by the equivalent amount of chlorine or bromine: acetic acid,  $\text{CH}_3\text{CO}(\text{OH})$ , for example, yields monochloracetic,  $\text{CH}_2\text{ClCO}(\text{OH})$ , dichloracetic,  $\text{CHCl}_2\text{CO}(\text{OH})$ , and trichloracetic,  $\text{CCl}_3\text{CO}(\text{OH})$  acid. These haloid derivatives yield metallic and ethereal salts, acid chlorides, acid amides, &c. The acids of the acrylic, sorbic, cinnamic, and fumaric series combine directly with chlorine and bromine.

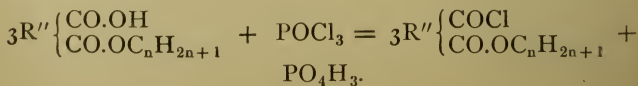
*Acid Chlorides, Bromides, and Iodides* are the products of the action of the haloid phosphorus compounds on the acids or their metallic salts, and are formed by the replacement of (OH) in the  $\text{CO}(\text{OH})$  group by chlorine, bromine, or iodine:



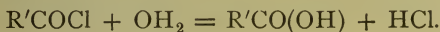
The first action of the haloid phosphorus compound on the dibasic acids doubtless consists in the production of an unstable compound intermediate between the acid and the acid chloride above formulated, but which cannot be isolated, since on heating it is resolved into the acid anhydride and haloid acid, thus:



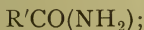
The ethereal salts of these intermediate compounds are readily obtained, however, by the action of the haloid phosphorus compounds on the acid ethereal salts of the polybasic acids; for example:



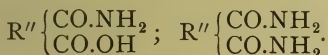
The acid chlorides, &c. are readily decomposed by water, with formation of the acid employed in their preparation and haloid acid :



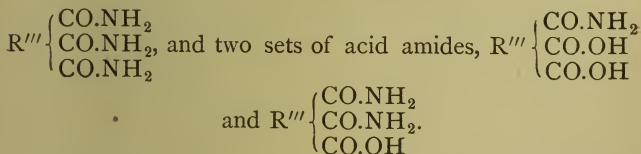
*Acid Amides.*—These compounds may be regarded as formed from the acids by the replacement of (OH) in the carboxyl group by the monad residue (NH<sub>2</sub>), derived from ammonia by the withdrawal of one unit of hydrogen. *Normal amides*, and *acid amides* or *amic acids* are to be distinguished. The monobasic acids yield only compounds of the former class, represented by the general expression



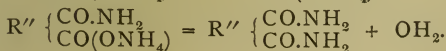
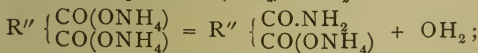
the dibasic acids yield acid and normal amides of the form



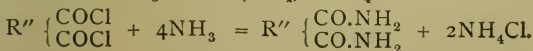
Similarly, the tribasic acids yield normal amides of the form



*Preparation.*—1. By distillation of the ammoniac salts of the acids :

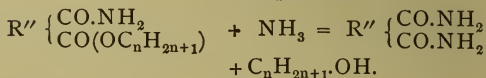
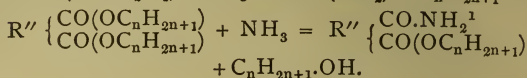
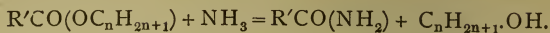


2. By the action of the acid chlorides on ammonia :

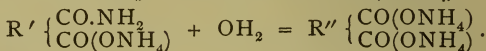
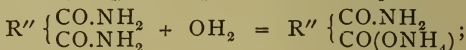




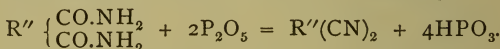
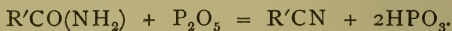
3. By the action of ammonia on the ethereal salts of the acids :



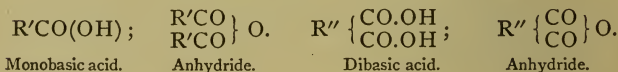
The acid amides are converted more or less readily on heating with water into the ammoniac salt of the parent acid :



On distillation with phosphoric anhydride they are converted into cyano-derivatives of hydrocarbons (so-called *nitriles*) :



*Acid Anhydrides*.—These compounds bear the same relation to the acids that the ethers bear to the alcohols :



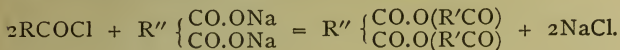
*Preparation*.—I. The anhydrides of monobasic acids are produced by the action of the acid chlorides on the acids or their metallic salts :



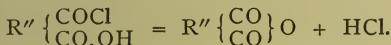
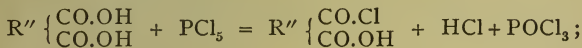
By acting upon the metallic salt of an acid by an acid chloride derived from a different acid, various so-called mixed anhydrides are formed ; and similarly, by the action of the acid chlorides derived from the monobasic acids on the metallic salts

<sup>1</sup> Ethereal salt of amic acid.

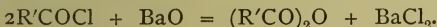
of polybasic acids, mixed anhydrides derived from a monobasic and a polybasic acid are obtained; for example:



The anhydrides of polybasic acids are produced by the action of phosphorus pentachloride on the acids; thus:



2. Anhydrides are also obtained by the action of acid chlorides on metallic oxides:



*Properties.*—In contact with water the anhydrides are converted into the corresponding acids. By the action of phosphorus pentachloride they are converted into acid chlorides:

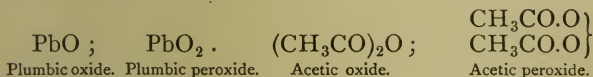


By their action on the alcohols ethereal salts are produced.

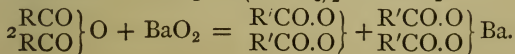
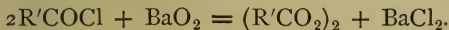


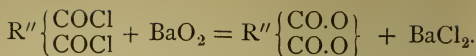
Similarly, the action of ammonia gives rise to the formation of acid amides.

*Acid Peroxides.*—These compounds bear the same relation to the acid anhydrides that the metallic oxides bear to the metallic peroxides, thus:



They are formed by the action of the acid chlorides or anhydrides on the metallic peroxides (preferably baric peroxide):





The acid peroxides are exceedingly unstable bodies, and, like the metallic peroxides, are powerful oxidising agents.

$\text{C}_n\text{H}_{2n+1}\text{CO}(\text{OH})$  OR ACETIC SERIES OF MONOBASIC ACIDS.

The following terms of the series are known :—

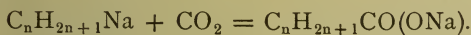
|                              |   |   |                                                  |
|------------------------------|---|---|--------------------------------------------------|
| Methylic or Formic acid      | . | . | $\text{HCO}(\text{OH})$                          |
| Ethylic or Acetic acid       | . | . | $\text{CH}_3\text{CO}(\text{OH})$                |
| Propylic or Propionic acid   | . | . | $\text{C}_2\text{H}_5\text{CO}(\text{OH})$       |
| Tetrylic or Butyric acid     | . | . | $\text{C}_3\text{H}_7\text{CO}(\text{OH})$       |
| Pentylic or Valeric acid     | . | . | $\text{C}_4\text{H}_9\text{CO}(\text{OH})$       |
| Hexylic or Caproic acid      | . | . | $\text{C}_5\text{H}_{11}\text{CO}(\text{OH})$    |
| Heptylic or Cœnanthylic acid | . | . | $\text{C}_6\text{H}_{13}\text{CO}(\text{OH})$    |
| Octylic or Caprylic acid     | . | . | $\text{C}_7\text{H}_{15}\text{CO}(\text{OH})$    |
| Nonylic or Pelargonic acid   | . | . | $\text{C}_8\text{H}_{17}\text{CO}(\text{OH})$    |
| Capric acid                  | . | . | $\text{C}_9\text{H}_{19}\text{CO}(\text{OH})$    |
| Lauric acid                  | . | . | $\text{C}_{11}\text{H}_{23}\text{CO}(\text{OH})$ |
| Myristic acid                | . | . | $\text{C}_{13}\text{H}_{27}\text{CO}(\text{OH})$ |
| Palmitic acid                | . | . | $\text{C}_{15}\text{H}_{31}\text{CO}(\text{OH})$ |
| Stearic acid                 | . | . | $\text{C}_{17}\text{H}_{35}\text{CO}(\text{OH})$ |
| Arachidic acid               | . | . | $\text{C}_{19}\text{H}_{39}\text{CO}(\text{OH})$ |
| Behenic acid                 | . | . | $\text{C}_{21}\text{H}_{43}\text{CO}(\text{OH})$ |
| Cerotic acid                 | . | . | $\text{C}_{26}\text{H}_{55}\text{CO}(\text{OH})$ |
| Melissic acid                | . | . | $\text{C}_{29}\text{H}_{59}\text{CO}(\text{OH})$ |

*Occurrence.*—Many of these acids are met with in nature : some in the free state, as, for example, formic acid in ants (*formica*) and the nettle, valeric acid in the valerian root, pelargonic acid in *Pelargonium roseum*, and cerotic acid in bees-wax. Others are present in the form of ethereal salts : thus, the essential oils obtained from the seeds of various species of Umbelliferæ<sup>1</sup> contain octylic acetate and hexylic butyrate ; spermaceti, which is a crystalline substance

<sup>1</sup> From *Heracleum spondylium*, the common cow-parsnep ; *Pastinaca sativa*, the edible parsnep ; and *Heracleum giganteum*.

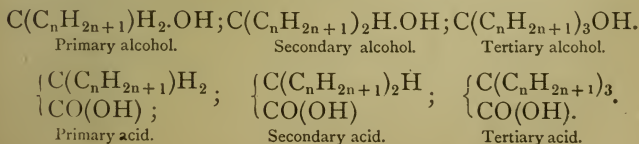
found in cavities in the head of the sperm whale, is a cetylic palmitate. The natural fats are mainly composed of glyceric ethereal salts of the acids of the acetic series : thus mutton and beef fat contain glyceric stearate, and palm oil is in the main a glyceric palmitate. The first nine terms of the series have also been prepared by various synthetic processes, and of most of these several isomeric modifications are known. Our knowledge of the remaining terms, of which isomerides are not known to exist, is derived from the study of substances isolated from natural products. On account of the oily or fatty character of the higher terms of the series, these acids are commonly designated the fatty series of acids.

*Preparation.*—The four general methods already noticed (p. 241) are all available. A fifth method, to which great interest attaches, consists in acting upon the sodium organo-metallic compounds of the form  $C_nH_{2n+1}Na$  with carbonic anhydride, when a sodium salt of an acid of the series is produced :



Various special methods are also employed in the preparation of individual members of the series.

*Classification of Isomeric Acids.*—The same system may be adopted as in the case of the aldehydes and alcohols, and the various isomeric acids classed as normal or iso-primary, normal or iso-secondary or tertiary, according as they are obtained by the fourth general method from normal or iso-primary, normal or iso-secondary or tertiary alcohols, or by the third general method from haloid derivatives of paraffins which, if converted into alcohols, would yield normal or iso-primary, normal or iso-secondary or tertiary alcohols ; thus :



*Properties.*—As in all other homologous series the boiling-point, specific gravity, and solubility in water vary as the series is ascended. The lowest terms are mobile, colourless liquids, which readily dissolve in water, but as the complexity increases the successive terms become gradually less mobile and less soluble in water; and the highest terms are fatty, solid substances, almost insoluble in water. The specific gravity decreases from term to term. Each addition of  $\text{CH}_2$  corresponds in the case of the first few terms of the normal primary series to a rise of about  $22^\circ$  in boiling-point; this difference diminishes gradually as the series is ascended, as will be evident on inspection of the accompanying table, but as at present determined the boiling points of the higher terms are somewhat irregular. The highest terms cannot be distilled unchanged under the ordinary atmospheric pressure, but may be under reduced pressure.

FORMIC or METHYLIC ACID (*Hydric Formate*),  $\text{CH}_2\text{O}_2 = \text{HCO}(\text{OH})$ .—Formic acid is formed in small quantity on passing the silent electric discharge through a mixture of carbonic anhydride and hydrogen (Brodie):  $\text{CO}_2 + \text{H}_2 = \text{CH}_2\text{O}_2$ ; it is produced by oxidation of methylic alcohol, and also by oxidation of various organic substances, such as starch, sugar, gum, &c. Potassic formate is produced by digesting together at  $100^\circ$  for some hours, moist potassic hydrate and carbonic oxide:  $\text{CO} + \text{KHO} = \text{HCO}(\text{OK})$ ; by exposing potassium in an atmosphere of moist carbonic anhydride; by digesting hydrocyanic acid with potassic hydrate solution, and by the action of potassic hydrate on trichloromethane,  $\text{CHCl}_3 + 4\text{KHO} = \text{HCO}(\text{OK}) + 3\text{KCl} + 2\text{OH}_2$ . It is usually prepared by heating a mixture of about equal weights of oxalic acid and glycerin with a little water to a temperature not exceeding about  $110^\circ$ ; so soon as effervescence ceases, water is added, and the mixture distilled until the temperature rises to about  $110^\circ$ , when more water is added, and the distillation continued. These operations are repeated so long as formic acid passes



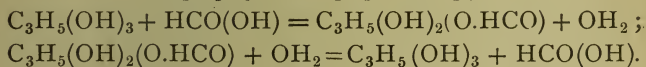


## Table of Homologous and Isomeric Acids of the Acetic Series.

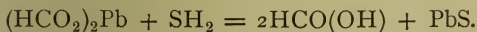
| NORMAL PRIMARY ACIDS.                                                                                                                                                                        |                                 |              | ISOPRIMARY ACIDS.                                                                                                                                            |       |            | NORMAL SECONDARY ACIDS.                                                                                                               |       |            | NORMAL TERTIARY ACIDS.                                                                                                      |       |         |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|--------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|------------|---------------------------------------------------------------------------------------------------------------------------------------|-------|------------|-----------------------------------------------------------------------------------------------------------------------------|-------|---------|
|                                                                                                                                                                                              | B.-P.                           | Sp. Gr.      |                                                                                                                                                              | B.-P. | Sp. Gr.    |                                                                                                                                       | B.-P. | Sp. Gr.    |                                                                                                                             | B.-P. | Sp. Gr. |
| $\begin{Bmatrix} \text{H} \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Formic acid                                                                                                              | 100°                            | 1'23 at 16°  |                                                                                                                                                              |       |            |                                                                                                                                       |       |            |                                                                                                                             |       |         |
| $\begin{Bmatrix} \text{CH}_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Acetic acid                                                                                                           | 118°                            | 1'002 at 20° |                                                                                                                                                              |       |            |                                                                                                                                       |       |            |                                                                                                                             |       |         |
| $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Propionic (methacetic) acid                                                                         | 140°·5                          | '996 at 19°  |                                                                                                                                                              |       |            |                                                                                                                                       |       |            |                                                                                                                             |       |         |
| $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Butyric (ethacetic) acid                                                          | 162°–163°                       | '981 at 0°   | —                                                                                                                                                            | —     | —          | $\begin{Bmatrix} \text{CH}(\text{CH}_3)_2 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Isobutyric (dimethacetic) acid                    | 154°  | '959 at 0° |                                                                                                                             |       |         |
| $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Valeric (propacetic) acid                                       | 185°                            | '957 at 0°   | $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Isovaleric (isopropacetic) acid                        | 175°  | '946 at 0° | $\begin{Bmatrix} \text{CH}(\text{CH}_3)(\text{C}_2\text{H}_5) \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Optically active valeric acid | 173°  | —          | $\begin{Bmatrix} \text{C}(\text{CH}_3)_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Trimethacetic acid                       | 163°  | —       |
| $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Caproic or hexylic acid                       | 205°                            | '943 at 0°   | $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Isocaproic acid                      | 199°  | —          | $\begin{Bmatrix} \text{CH}(\text{C}_2\text{H}_5)_2 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Diethacetic acid                         | 196°  | —          | $\begin{Bmatrix} \text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Dimethethacetic acid | 187°  | —       |
| $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Enanthylic or heptylic acid | 223°–224°                       | '934 at 0°   | $\begin{Bmatrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2 \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Isoamylacetic acid | —     | —          |                                                                                                                                       |       |            |                                                                                                                             |       |         |
| $\begin{Bmatrix} (\text{C}_7\text{H}_{15})^a \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Octylic or caprylic acid                                                                              | 237°–240° ?<br>Melts at 15°–16° |              |                                                                                                                                                              |       |            |                                                                                                                                       |       |            |                                                                                                                             |       |         |
| $\begin{Bmatrix} (\text{C}_8\text{H}_{17})^a \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Nonylic or pelargonic acid                                                                            | 253°–254° ?<br>Melts at 12°     | '9065 at 17° |                                                                                                                                                              |       |            |                                                                                                                                       |       |            |                                                                                                                             |       |         |
| $\begin{Bmatrix} (\text{C}_9\text{H}_{19})^a \\ \text{CO}(\text{OH}) \end{Bmatrix}$<br>Decylic or capric acid.                                                                               | 268°–270° ?<br>Melts at 30°     |              |                                                                                                                                                              |       |            |                                                                                                                                       |       |            |                                                                                                                             |       |         |

The acids which figure in this table which are not described in the text are derived from the following, amongst other sources:—*Caproic* or *hexylic acid* is produced—1. by oxidation of normal primary hexylic alcohol from *heracleum oil* (p. 250), &c.; 2. by method 4 (p. 242) from normal primary amylalcohol; and, 3. together with acetic and butyric acids, by fermentation of lactic acid (p. 202). *Enanthylic* or *heptylic acid* has been prepared by method 4 from normal primary hexylic alcohol; and, 2. by oxidation of *enanthylic aldehyde* (emanthol, p. 285). *Octylic* or *caprylic acid* is the oxidation-product of normal primary octylic alcohol from *heracleum oil*, &c.; it is present in cocoa-nut oil. *Nonylic acid* has been prepared from normal primary octylic alcohol by method 4. *Decylic* or *capric acid* is present as ethylic salt in Hungarian wine fusel oil. It is not yet placed beyond doubt that the two latter acids are normal primary and not isoprimary acids. *Isocaproic acid* is prepared by method 4 from isoprimary (fermentation) amylalcohol. *Isoamylacetic acid* was obtained by Frankland and Duppa by the action of iso(primary)amyl iodide, and *diethacetic acid* by the action of ethylic iodide, on the product of the action of sodium on ethylic acetate (p. 256). A fourth hexylic acid—*methisopropacetic acid*,  $\begin{Bmatrix} \text{CH}(\text{CH}_3) \cdot \text{CH}(\text{CH}_3)_2 \\ \text{CO}(\text{OH}) \end{Bmatrix}$ , the only known isosecondary acid—has been prepared by method 4 from methylisopropylcarbinol.

over with the water, when a fresh quantity of oxalic acid may be similarly decomposed. Oxalic acid when heated alone is resolved into carbonic anhydride and formic acid, although at a comparatively high temperature, and much of the formic acid is broken up into water and carbonic oxide ; in presence of glycerin, however, the decomposition commences below  $50^{\circ}$ , and is perfect below  $110^{\circ}$ , little or no carbonic oxide being formed. The glycerin appears to promote the decomposition of the oxalic acid, in virtue of the tendency which it has to react with the formic acid, the product of this reaction (monoformin) being subsequently decomposed on distillation with water ; thus :



A relatively small amount of glycerin is thus able to effect the conversion of a large quantity of oxalic acid into formic acid. To prepare anhydrous formic acid from the product, it is neutralised with plumbic carbonate, evaporated to dryness, and the dry plumbic formate heated gently in a current of hydric sulphide gas :



Formic acid is a colourless, inflammable, highly corrosive liquid, of sp. gr. 1.235, possessing an extremely penetrating odour, soluble in water in all proportions ; it boils at about  $100^{\circ}$ . Cooled to a temperature below  $0^{\circ}$ , it crystallises in large brilliant plates. It is a powerful reducing agent, being most readily oxidised to carbonic anhydride and water ; thus it precipitates metallic silver from a solution of argentic nitrate ; it reduces mercuric to mercurous chloride, and mercuric oxide to metallic mercury :  $\text{CH}_2\text{O}_2 + \text{HgO} = \text{CO}_2 + \text{OH}_2 + \text{Hg}$ . This behaviour serves to distinguish formic acid from the remaining terms of the series, which are only oxidised with difficulty.

The metallic salts of formic acid (formates) are all soluble in water.

ACETIC or ETHYLIC ACID (*Hydric Acetate*),  $C_2H_4O_2 = CH_3CO(OH)$ .—This acid is present in small quantity in the juices of many plants, and in various animal fluids. It is produced by the general methods previously described from ethylic alcohol, ethylic aldehyde, ethane, methylic alcohol, and sodic methide,  $CH_3Na$ . A mixture of equal volumes of acetylene and oxygen in contact with a potassic hydrate solution is gradually absorbed, potassic acetate being formed :  $C_2H_2 + O + KHO = C_2H_3KO_2$ . On the large scale acetic acid is prepared by the destructive distillation of wood :—

Dry hard wood, usually beech or oak, is strongly heated in large iron retorts. Much inflammable gas is given off, an acid liquid and tar distil over, and charcoal remains in the retort. The acid liquid is distilled and the portion which first passes over, consisting chiefly of methylic alcohol, is collected apart; the crude acid which afterwards distils is saturated with slaked lime, and the solution of calcic acetate thus formed is mixed with a solution of sodic sulphate, whereby sodic acetate and insoluble calcic sulphate are produced. The solution of sodic acetate is evaporated to crystallisation, the crystals of the crude salt are dried and carefully fused in order to expel and decompose a quantity of adherent tarry matter, redissolved in water, and recrystallised. Finally, acetic acid is obtained by distilling the salt thus purified with sulphuric acid.

Acetic acid is a colourless, mobile, highly corrosive, pungent-smelling liquid, of sp. gr. 1.063 at  $15^\circ$ ; it solidifies at  $16.5^\circ$  to a white crystalline mass. Acetic acid boils at  $119^\circ$ . It is soluble in water in all proportions.

The density of the mixture increases until it becomes 1.073, which is the density of a mixture of 79 parts of the acid with 21 parts of water; all further additions of water diminish the density. This mixture boils under the ordinary atmospheric pressure constantly at  $104^\circ$ , undergoing scarcely any change in

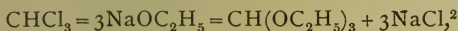
composition<sup>1</sup>; it about corresponds in composition to a hydrate of the formula  $C_2H_4O, H_2O$ . All the lower terms of the acetic series appear to behave similarly, and to furnish corresponding hydrates having fixed and constant boiling-points, which may be distilled almost unchanged in composition. These hydrates are apparently members of a well-defined though unstable class of compounds, which may be termed *ortho-acids*, represented by

the general formula  $C_nH_{2n+1}C \begin{Bmatrix} (OH) \\ (OH) \\ (OH) \end{Bmatrix}$ ; they bear the same rela-

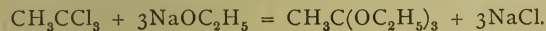
tion to the acids of the form  $C_nH_{2n+1}CO(OH)$  that the hydrates of the aldehydes of the acetic series of the form

$C_nH_{2n+1}C \begin{Bmatrix} H \\ (OH) \\ (OH) \end{Bmatrix}$  bear to the aldehydes of the form  $C_nH_{2n+1}COH$ .

This view is confirmed by the fact that ethereal salts derived from these ortho-acids are known which are relatively very stable substances, not undergoing the slightest decomposition when distilled, such as *ethylic orthoformate*, obtained by the action of sodic ethylate on trichloromethane :



and *ethylic orthoacetate* similarly prepared from trichlorethane :



*Metallic Acetates*.—The normal acetates are readily obtained by dissolving the metallic carbonates in acetic acid ;

<sup>1</sup> If a mixture containing more or less than about 20 per cent. of water be distilled, water, or acetic acid, passes over until a mixture of the composition indicated is formed, which then distils unchanged. The relative proportions in which the acid and water are contained in a mixture having a constant boiling-point and passing over unchanged on distillation varies with the pressure, however, owing to the more or less complete dissociation of the hydrate,  $C_2H_4O_2, OH_2$ ; under the higher pressure the mixture has a higher boiling-point and contains relatively more acid than under the lower pressure.

<sup>2</sup> Hydric orthoformate is doubtless an intermediate product in the formation of potassic formate from potassic hydrate and trichloromethane (p. 252); thus :



the acid salts (page 243) or so-called diacetates are prepared by evaporating the acetates of the alkali metals with an excess of acetic acid ; these diacetates are resolved on heating strongly into an acetate and acetic acid, and may, in fact, conveniently be employed in the preparation of anhydrous acetic acid. Basic acetates are produced by digesting metallic acetates with excess of metallic oxide ; for example, by digesting a solution of plumbic acetate with plumbic oxide, the two basic salts  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Pb} \cdot \text{PbO}$  and  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Pb} \cdot 2\text{PbO}$  are formed.

*Ethereal Acetates.*—These derivatives are produced by the general methods already described. The following have been obtained from acetic acid and monohydric alcohols of the ethylic series :—

|                      |                                                      | B.-P.                 |
|----------------------|------------------------------------------------------|-----------------------|
| Methylic acetate .   | $\text{CH}_3\text{CO}(\text{OCH}_3)$ .               | $55^\circ.5$          |
| Ethylic acetate .    | $\text{CH}_3\text{CO}(\text{OC}_2\text{H}_5)$ .      | $77^\circ$            |
| Propylic acetate .   | $\text{CH}_3\text{CO}(\text{OC}_3\text{H}_7^a)$ .    | $102^\circ$           |
| Isopropylic acetate  | $\text{CH}_3\text{CO}(\text{OC}_3\text{H}_7^b)$ .    | $90^\circ-93^\circ$   |
| Butylic acetate .    | $\text{CH}_3\text{CO}(\text{OC}_4\text{H}_9^a)$ .    | $125^\circ$           |
| Isobutylic acetate . | $\text{CH}_3\text{CO}(\text{OC}_4\text{H}_9^b)$ .    | $117^\circ.5$         |
| Amylic acetate .     | $\text{CH}_3\text{CO}(\text{OC}_5\text{H}_{11}^a)$ . | $149^\circ$           |
| Isoamylic acetate .  | $\text{CH}_3\text{CO}(\text{OC}_5\text{H}_{11}^b)$ . | $138^\circ-140^\circ$ |

They are colourless, mobile, fragrant liquids ; isoamylic acetate possesses in a remarkable degree the odour of the Jargonelle pear, and on that account is largely used for flavouring confectionery.

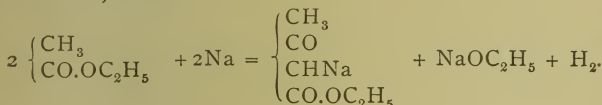
*Action of Sodium on Ethylic Acetate (Acetic Ether).*—This reaction has received investigation at the hands of various chemists, and has given rise to considerable discussion. Frankland and Duppa and Geuther, to whom we are indebted for our knowledge of the subject, have always observed the evolution of hydrogen, which they regard as an essential product of the reaction ; whereas, according to Wanklyn, no hydrogen is evolved by the action of sodium on *pure* ethylic acetate, and this statement has been confirmed by Ladenburg. Wanklyn maintains



that the production of hydrogen is the result of a secondary action; that it is, in fact, a product of the action of the sodium on the alcohol which is always contained to a greater or less extent in ethylic acetate prepared by the ordinary methods.

The action of sodium on ordinary ethylic acetate takes place readily, commencing at a temperature considerably below its boiling-point; but ethylic acetate free from alcohol, according to Ladenburg, is only acted upon with difficulty and on prolonged heating at 100°. These observations suggest the query, whether the presence of alcohol is not essential to start the action in the first instance.

According to Geuther, when sodium is added to a large excess<sup>1</sup> of ethylic acetate, the sole product besides hydrogen and sodic ethylate is a body of the composition  $C_6H_9NaO_3$ , which he regards as the sodic salt of an acid termed by him *ethyl-diacetic acid*. Judging from its reactions, however, there can be no doubt but that it is simply the sodium-derivative of an ethylic acetoacetate,<sup>2</sup> thus:



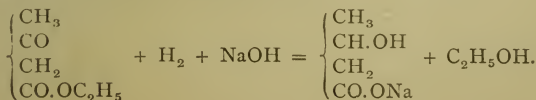
In Frankland and Duppa's experiments the sodium was

<sup>1</sup> If a relatively small quantity of ethylic acetate be taken, the first product is liable to undergo change during the prolonged heating which is then necessary to effect the complete solution of the sodium.

<sup>2</sup> By treating the compound  $C_6H_9NaO_3$  with acetic acid Geuther has succeeded in replacing the sodium by hydrogen. Ethylic acetoacetate thus formed is an oily liquid, boiling at about 181°; on heating with water and an alkali it is resolved into *acetone*, alcohol, and a metallic carbonate, thus:

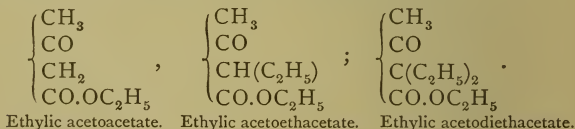


By the action of sodium amalgam on an aqueous solution of ethylic acetoacetate the sodic salt of  $\beta$ -oxybutyric acid is produced:



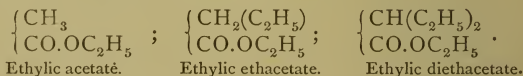


placed in a vessel connected with a flask—containing the ethylic acetate—heated in an oil-bath, and with a condenser, the apparatus being so arranged that the vapour passed over the surface of the sodium and thence into the condenser, where it was liquefied; the condensed liquid then dropped on to the surface of the sodium and ran back into the heated flask. The solid product was thus dissolved off the sodium almost as rapidly as it was formed, and a fresh surface continuously exposed to the action of the ethylic acetate. In this manner they were able to dissolve an amount of sodium only slightly less than is indicated by the proportion  $\text{CH}_3\text{CO}.\text{OC}_2\text{H}_5 : \text{Na}$ . The contents of the flask were then introduced into a digester, an amount of ethylic iodide added equivalent to the amount of sodium employed, and the digester heated during several hours to  $100^\circ$ ; after cooling, a considerable quantity of water was added, and the whole submitted to distillation in an oil-bath. At first ethylic ether, together with some unattacked ethylic acetate, passed over; but afterwards, as the temperature rose, an oily liquid came over with the water; this was separated by fractional distillation into four distinct compounds. Two of these, termed by Frankland and Duppa *ethylic ethacetone carbonate* and *ethylic diethacetone carbonate*, are respectively the monethyl- and diethyl-derivative of the ethylic acetoacetate above mentioned, thus:



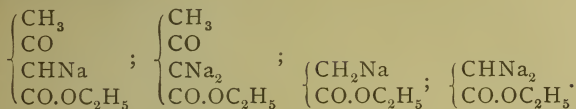
Ethylic acetoethacetate has been obtained by Geuther by the action of ethylic iodide on the compound  $\text{C}_6\text{H}_9\text{NaO}_3$ .

The remaining products are the ethylic salts of *ethacetic* (butyric) and *diethacetic* (caproic) acid:



Frankland and Duppa thought that each of these four products is formed by the action of ethylic iodide on a corresponding sodium-derivative; in fact, that the action of sodium on

ethylic acetate gives rise to at least four distinct sodium compounds, namely :

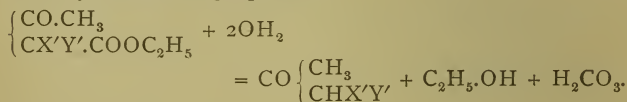


Geuther maintained, however, that the compound  $\text{C}_6\text{H}_9\text{NaO}_3$  (ethylic acetosodacetate) is the only sodium-derivative produced, and that the various products obtained by Frankland and Duppa are to be regarded as formed from the ethylic derivative of this compound by the action of sodic ethylate.

The more recent researches of Wislicenus have confirmed Geuther's conclusions as to the nature of the reaction between sodium and ethylic acetate, and show that the bodies obtained by Frankland and Duppa are formed in the following manner. In the first instance the ethylic acetate is converted into ethylic acetosodacetate in accordance with the first equation on p. 257, sodic ethylate being formed simultaneously. On the addition of ethylic iodide, however, the ethylic acetosodacetate is converted into *ethylic acetoethacetate*,  $\text{CH}_3\text{.CO.CH(C}_2\text{H}_5\text{).COOC}_2\text{H}_5$ , but this compound is at once partially acted upon by the sodic ethylate and converted into *ethylic acetosodethacetate*,  $\text{CH}_3\text{.CO.CNa(C}_2\text{H}_5\text{).COOC}_2\text{H}_5$ , and this latter body, under the influence of the ethylic iodide still present, then partially exchanges its sodium for ethyl, thus giving rise to *ethylic aceto-diethacetate*,  $\text{CH}_3\text{.CO.C(C}_2\text{H}_5\text{)}_2\text{.COOC}_2\text{H}_5$ . Ethylic acetoacetate (foot-note, p. 257) may be converted into the acetosodacetate by warming with sodic ethylate as well as by the direct action of sodium, but it is not possible to replace more than a single unit of hydrogen by the metal; ethylic acetodiethacetate is not acted upon by sodium. The ethylic ethacetate and diethacetate are formed by the action of the sodic ethylate on ethylic acetoethacetate and acetodiethacetate; a complex mixture of products is obtained, and the precise character of the reaction has not been ascertained, but the chief result appears to be that the acetyl group,  $\text{CH}_3\text{.CO}$ , of the acetoacetate is simply displaced by hydrogen.

Wislicenus has shown that ethylic acetoacetate is a synthetic agent of the highest value : by acting on it with sodic ethylate

and treating the resulting acetosodacetate with a haloid compound such as a moniodoparaffin or ethylic monochloracetate,  $\text{CH}_2\text{Cl.COOC}_2\text{H}_5$ , or, in fact, any haloid compound which will exchange its halogen, a series of compounds may be obtained which may be represented by the general formula  $\text{CH}_3.\text{CO}.\text{CHX}'.\text{COOC}_2\text{H}_5$ ,  $\text{X}'$  being the radicle associated with the halogen in the haloid compound employed. By similarly treating these compounds, first with sodic ethylate and then with a haloid compound—which may be the same as, or different from, that first employed—a series of compounds of the form  $\text{CH}_3.\text{CO}.\text{CX}'\text{Y}'.\text{COOC}_2\text{H}_5$  are then obtained,  $\text{Y}'$  being the radicle of the haloid compound employed. When either of these two kinds of derivatives is heated with a solution of baric hydrate, it is almost entirely decomposed in the manner indicated by the following equation :



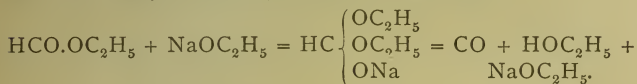
But if it is decomposed by means of a very concentrated alcoholic solution of potassic hydrate, the following decomposition also takes place :



So that on the one hand it is possible to obtain a series of mono- and di-derivatives of acetone,  $\text{CH}_3.\text{CO}.\text{CH}_3$ ; and on the other, a series of mono- and di-derivatives of acetic acid.

A number of observations which have been made on the action of sodic ethylate on various ethereal salts are of considerable interest when viewed in connection with the experiments on the action of sodium on ethylic acetate. Thus, on heating with sodic ethylate, ethylic formate,  $\text{HCO}.\text{OC}_2\text{H}_5$ , is resolved into carbonic oxide and alcohol; ethylic oxalate,  $\left\{ \begin{array}{l} \text{CO}.\text{OC}_2\text{H}_5 \\ \text{CO}.\text{OC}_2\text{H}_5 \end{array} \right.$ , is resolved into carbonic oxide and ethylic carbonate,  $\text{CO}(\text{OC}_2\text{H}_5)_2$ ; and ethylic carbonate yields ethylic ether and sodic ethylic carbonate,  $\text{CO} \left\{ \begin{array}{l} \text{ONa} \\ \text{OC}_2\text{H}_5 \end{array} \right.$ . A simple explanation of these decompositions is afforded if it be assumed that in the first

place the ethereal salt combines with the sodic ethylate, and that the compound so formed is subsequently decomposed; in the case of ethylic formate, for example, we have :



A small quantity of ethylate suffices thus to decompose a relatively large quantity of ethereal salt, and were it not that secondary products are formed, it would doubtless suffice to decompose an infinite quantity. Sodium effects a precisely similar decomposition, but it appears probable that the ethereal salt is not affected by the sodium as such, but rather that by the action of the latter on traces of alcohol present, sodic ethylate is produced, which then decomposes the ethereal salt in the manner indicated. It is interesting to note that no hydrogen is evolved by the action of sodium on ethylic formate containing a considerable proportion of alcohol; it would appear that it is consumed in the formation of secondary products, and that the reaction resembles that which occurs when nitric acid is acted upon by metals—in this case also, as a rule, no hydrogen is evolved, although the first action undoubtedly consists in the displacement of hydrogen in the acid by the metal, because it at once attacks the nitric acid and reduces it.

Ethylic acetoacetate readily exchanges one of its atoms of hydrogen for other metals besides sodium. Thus on shaking it with an ammoniacal solution of cupric sulphate, a pale green precipitate of *ethylic acetocupracetate*,  $(\text{C}_6\text{H}_9\text{O}_3)_2\text{Cu}$ , is obtained; and the corresponding magnesium derivative may be prepared in a similar manner, or by the action of magnesium amalgam. Both these compounds crystallise well from benzene. The former melts at  $182^\circ$ , the latter at  $240^\circ$ . The aluminium derivative  $(\text{C}_6\text{H}_9\text{O}_3)_3\text{Al}$ , forms glistening crystals, melting at  $76^\circ$ , and may even be distilled unchanged.

Ethylic acetoacetate is also readily acted upon by chlorine, and converted into the dichlorinated derivative  $\text{CH}_3.\text{CO}.\text{CCl}_2.\text{COOC}_2\text{H}_5$ .

On treatment with a dilute aqueous solution of nitrous acid, it forms the nitroso-derivative  $\text{CH}_3.\text{CO}.\text{CH}(\text{NO}).\text{COOC}_2\text{H}_5$ .

The introduction of the acetyl or  $\text{CH}_3.\text{CO}$  group in place of

one of the units of hydrogen in the  $\text{CH}_3$  group of ethylic acetate has, therefore, a most remarkable effect, rendering the two remaining units of hydrogen extremely mobile and readily displaceable both by positive and negative radicles.

*Haloid Substitution-derivatives of Acetic Acid.*—By the action of chlorine on boiling acetic acid to which some iodine has been added, it is converted into monochloroacetic acid, and if the action be prolonged, dichloroacetic acid is formed; trichloroacetic acid is obtained by the action of an excess of chlorine on acetic acid in sunlight, but it is best prepared by oxidation of chloral. Similarly, by heating acetic acid with bromine, mono- and dibromoacetic acid are obtained; tribromoacetic acid is obtained by oxidation of tribromoaldehyde (bromal). These acids are crystalline substances, which boil unchanged at temperatures higher than acetic acid :

|                                     | B.-P.             |                                     | B.-P.                         |
|-------------------------------------|-------------------|-------------------------------------|-------------------------------|
| $\text{CH}_3\text{CO}(\text{OH})$   | $119^\circ$       | $\text{CH}_2\text{BrCO}(\text{OH})$ | $208^\circ$                   |
| $\text{CH}_2\text{ClCO}(\text{OH})$ | $185^\circ$       | $\text{CHBr}_2\text{CO}(\text{OH})$ | $225^\circ\text{--}230^\circ$ |
| $\text{CHCl}_2\text{CO}(\text{OH})$ | $195^\circ$       | $\text{CBr}_3\text{CO}(\text{OH})$  | about $245^\circ$             |
| $\text{CCl}_3\text{CO}(\text{OH})$  | about $200^\circ$ |                                     |                               |

In chemical behaviour they resemble the parent substance, acetic acid, most closely, yielding metallic and ethereal salts, acid chloride, amides, &c. They are reconverted into acetic acid by the action of nascent hydrogen.

Haloid derivatives of most of the acids homologous with acetic acid have been prepared, but with few exceptions the mono-derivatives alone have been examined.

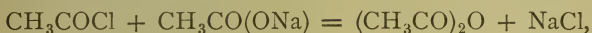
*Acetic Chloride (Acetyl Chloride)*,  $\text{CH}_3\text{COCl}$ .—This compound is best prepared by distilling a mixture of phosphorus trichloride and carefully dried acetic acid :



It is a mobile colourless liquid, possessing an extremely pungent odour like that of acetic and hydrochloric acid. It boils at  $55^\circ$ ; water decomposes it immediately, forming

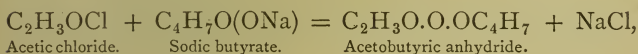
acetic and hydrochloric acid. Acetic bromide and iodide are analogous compounds.

*Acetic Anhydride*,  $\left. \begin{smallmatrix} \text{CH}_3\text{CO} \\ \text{CH}_3\text{CO} \end{smallmatrix} \right\} \text{O}$ , obtained by the action of acetic chloride on a metallic acetate—usually sodic or potassic acetate :



is a colourless mobile liquid, having a pungent odour similar to that of acetic acid. It boils at  $138^\circ$  ; when poured into water it forms oily drops which disappear after a while, the anhydride being converted into the acid.

Homologous compounds are similarly obtained from the acids homologous with acetic acid ; they exhibit an analogous behaviour. The mixed anhydrides formed by the action of the chloride of one acid on the metallic salt of another acid of the series—for example :



—cannot be distilled unchanged, but are resolved into two simple anhydrides :



*Acetic Peroxide*,  $\left. \begin{smallmatrix} \text{CH}_3\text{CO.O} \\ \text{CH}_3\text{CO.O} \end{smallmatrix} \right\}$ .—This compound is prepared by adding baric peroxide to a solution of acetic anhydride in anhydrous ether :



The ethereal solution is separated from the baric acetate by filtration, and cautiously evaporated ; the acetic peroxide then remains as a colourless viscid liquid. It is a powerful oxidising agent and violently explosive, and on this account is a most dangerous substance. Like chlorine it rapidly



bleaches indigo; it separates iodine from hydriodic acid and from potassic iodide; and it converts a solution of potassic ferrocyanide into potassic ferricyanide. The addition of baric hydrate solution to the peroxide suspended in water causes an immediate precipitation of hydrated baric peroxide.

*Thiacetic Acid*,  $\text{CH}_3\text{CO}(\text{SH})$ , is obtained by the action of acetic chloride on potassic sulphhydrate, or by distilling acetic acid with phosphorus pentasulphide,  $5\text{CH}_3\text{CO}(\text{OH}) + \text{P}_2\text{S}_5 = 5\text{CH}_3\text{CO}(\text{SH}) + \text{P}_2\text{O}_5$ . It is a colourless liquid, smelling like acetic and sulphydric acids together; it boils at  $95^\circ$ . Thiacetic acid decomposes metallic carbonates, forming metallic thiacetates,  $\text{CH}_3\text{CO}(\text{SM}')$ , &c. Phosphorus pentachloride converts it into acetic chloride:



By acting upon the metallic thiacetates with iodine, *acetic disulphide*—the sulphur analogue of acetic peroxide—is obtained:  $2\text{CH}_3\text{CO}(\text{SM}') + \text{I}_2 = 2\text{MI} + (\text{CH}_3\text{CO})\text{S}_2$ . *Acetic sulphide*,  $(\text{CH}_3\text{CO})_2\text{S}$ , is produced by distilling acetic anhydride with phosphorus pentasulphide.

*Acetamide*,  $\text{CH}_3\text{CO}(\text{NH}_2)$ , is most conveniently prepared by distillation of ammoniac acetate:  $\text{CH}_3\text{CO}(\text{ONH}_4) = \text{OH}_2 + \text{CH}_3\text{CO}(\text{NH}_2)$ ; it is also readily obtained by the action of ammonia on ethylic acetate, or acetic chloride. Acetamide is a white crystalline solid, which melts at  $78^\circ$  and boils unchanged at  $221^\circ$ ; it is readily soluble in water; on heating with water it is rapidly converted into ammoniac acetate. Acetamide combines with acids: thus with hydrochloric acid it forms the compound  $\text{CH}_3\text{CO}(\text{NH}_2)$ ,  $\text{HCl}$ ; it also yields metallic derivatives, such as  $\text{CH}_3\text{CO}(\text{NHAg})$ , *argentacetamide*, and  $\text{CH}_3\text{CO}(\text{NHg})$ , *mercuracetamide*. On distilling acetamide with phosphoric anhydride, methylic cyanide,  $\text{CH}_3\text{CN}$  (*acetonitrile*), is produced. The acid amides derived from the homologues of acetic acid are in every respect compounds analogous to acetamide.

*Derivatives formed from the haloid substitution-derivatives of Acetic Acid (and its homologues) by double decomposition.*—The haloid derivatives of acetic acid (and of its homologues) are capable of entering into reaction with various compounds to form, by double decomposition, new products which may equally well be regarded as substitution-derivatives (see *cyanacetic acid*, *glycollic acid*, *thioglycollic acid*). The behaviour of the mono-derivatives has received the greatest share of attention; little is known of the higher haloid substitution-derivatives, which appear to comport themselves in a somewhat different and peculiar manner.

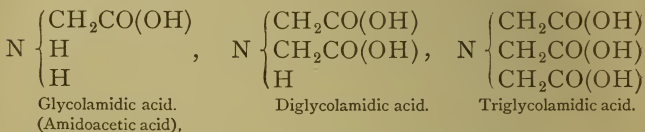
Special interest attaches to the compounds formed by the action of ammonia and the amines on the mono-haloid derivatives of acetic acid and its homologues, since many are identical with natural products. Hippuric acid, for example, a substance present in considerable quantity in the urine of the herbivora, is resolved on boiling with water and hydrochloric acid into benzoic acid and *glycocine* (glycocol),  $C_9H_9NO_3 + OH_2 = C_7H_6O_2 + C_2H_5NO_2$ ; and by heating monochlor- or bromacetic acid with ammonia, the ammoniac salt of *amidoacetic acid* is produced:  $CH_2ClCO(OH) + 3NH_3 = CH_2(NH_2)CO(OH) + NH_4Cl$ , the which amidoacetic acid is found to be in all respects identical with *glycocine* from hippuric acid.<sup>1</sup> Similarly, *amidocaproic acid*,  $C_5H_{10}(NH_2)CO(OH)$ , obtained by the action of ammonia on bromocaproic acid, is identical with *leucine*, a substance present in various parts of the animal organism (the brain, liver, and pancreas) and which is also formed when albumenoid matters of animal origin, such as horn, wool, &c. are heated with dilute acids or alkalis. Again, by the action of methylamine,  $NH_2(CH_3)$ , on chloracetic acid, *methylamidoacetic acid*,  $CH_2(NHCH_3)CO(OH)$ , is obtained, which is identical with *sarcosine*,<sup>2</sup> a product of the

<sup>1</sup> Hippuric acid has been obtained by heating *glycocine* with benzoic acid.

<sup>2</sup> Creatine has been produced by direct union of *sarcosine* and cyanamide ( $NH_2.CN$ ).

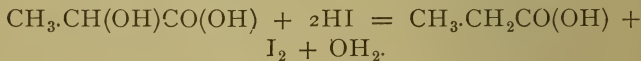
decomposition of creatine (a substance present in small quantity in flesh) by boiling with baric hydrate solution.

Amidoacetic acid is not the only compound formed by the action of ammonia on chloracetic acid, but the product is a mixture of the three bodies :



Monamido-derivatives of the acids of the acetic series are also produced by combining the aldehydes of the acetic series with ammonia, digesting the aldehyde-ammonias so formed with hydrocyanic acid, and subsequently heating the product with hydrochloric acid solution (see page 220). Thus acetic aldehyde is in this way converted into amido-propionic acid (*alanine*); and valeric aldehyde (from fermentation amylic alcohol) yields amidocaproic acid or *leucine*.

PROPYLIC or PROPIONIC ACID (*Methacetic Acid*),  $\text{C}_3\text{H}_6\text{O}_2 = \text{C}_2\text{H}_5\text{CO}(\text{OH}) = \text{CH}_3.\text{CH}_2\text{CO}(\text{OH})$ .—This acid is obtained by the general methods ; also as ethylic salt among the products of the action of methylic iodide on the product of the action of sodium on ethylic acetate ; and by heating lactic acid with hydriodic acid :



Propionic acid boils at  $140^\circ.5$  and in all respects closely resembles acetic acid.

TETRYLIC or BUTYRIC ACID,  $\text{C}_4\text{H}_8\text{O}_2 = \text{C}_3\text{H}_7\text{CO}(\text{OH})$ .—Two modifications of this acid are known—*normal* and *isobutyric acid*.

*Normal Butyric (Ethacetic) Acid*,  $\text{CH}_3.\text{CH}_2.\text{CH}_2\text{CO}(\text{OH})$ , is obtained on oxidation of normal primary butylic alcohol ; from normal primary propane ; from propylic alcohol (method 1, page 241) ; and as ethylic salt among the products

of the action of ethylic iodide on the product of the action of sodium on ethylic acetate. It is best prepared by allowing a mixture of sugar, chalk, and cheese to ferment (page 202). It is present in small quantity (as glyceric salt) in butter; also in perspiration, in the juice expressed from human flesh, and in various plants—usually in the form of an ethereal salt.

Normal butyric acid closely resembles acetic acid in appearance, but has a peculiar rancid odour; it boils at  $162^{\circ}$ – $163^{\circ}$ , and at  $0^{\circ}$  has the sp. gr.  $\cdot 981$ ; it is readily soluble in water.

*Isobutyric Acid* (*Dimethacetic Acid*),  $\text{CH}(\text{CH}_3)_2\text{CO}(\text{OH})$ , is obtained on oxidation of isoprimary (fermentation) butylic alcohol; from isopropylic alcohol; and as ethylic salt among the products of the action of methylic iodide on the product of the action of sodium on ethylic acetate. It resembles its isomeride in appearance, but boils at  $154^{\circ}$ , and at  $0^{\circ}$  has the sp. gr.  $\cdot 959$ ; moreover, calcic isobutyrate has the composition  $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, 5\text{OH}_2$ , whereas calcic butyrate is  $(\text{C}_4\text{H}_7\text{O}_2)_2\text{Ca}, \text{OH}_2$ ; the latter is more soluble in cold water than calcic isobutyrate, and is also characterised by being less soluble in hot than in cold water, so that if a cold saturated solution be warmed to  $70^{\circ}$ – $80^{\circ}$  the salt separates out in glistening crystalline plates. Similar differences exist between the derivatives of the two acids. Thus *isobutylic butyrate*,  $\text{C}_3\text{H}_7^{\alpha}\text{CO}(\text{OC}_4\text{H}_9^{\beta})$ , boils at  $150^{\circ}$ , and at  $0^{\circ}$  has the sp. gr.  $\cdot 8798$ , whilst *isobutylic isobutyrate*,  $\text{C}_3\text{H}_7^{\beta}\text{CO}(\text{OC}_4\text{H}_9^{\beta})$ , boils under similar conditions at  $144^{\circ}$ – $147^{\circ}$ , and at  $0^{\circ}$  has the sp. gr.  $\cdot 8757$ .

Both modifications are oxidised by prolonged heating with chromic acid solution, and yield the same products, namely, acetic acid and carbonic anhydride; but the normal acid is much less readily acted upon than is the iso-acid.

PENTYLIC OR VALERIC ACID,  $\text{C}_5\text{H}_{10}\text{O}_2 = \text{C}_4\text{H}_9\text{CO}(\text{OH})$ .—Four isomeric modifications of this acid exist.

*Normal Primary Valeric or Valerianic Acid* (*Propylacetic*

*Acid*),  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{CO}(\text{OH})$ , may be obtained by oxidation of normal primary amylic alcohol prepared from normal primary pentane, and from normal primary butylic alcohol (method 4, page 242). It closely resembles butyric acid in odour, but is more oily and less soluble in water. It boils at  $185^\circ$ , and at  $0^\circ$  has the sp. gr. '9577.

*Isoprimary Valeric Acid*,  $\text{CH}(\text{CH}_3)_2\cdot\text{CH}_2\text{CO}(\text{OH})$ , also known as *Isopropylacetic Acid*, is obtained on oxidation of the optically inactive isoprimary amylic alcohol of fermentation; from isoprimary butylic alcohol (method 4, page 242); and as ethylic salt among the products of the action of isopropyl iodide on the product of the action of sodium on ethylic acetate. It boils at  $175^\circ$ , and at  $0^\circ$  has the sp. gr. '9468.

The third modification is obtained by oxidation of the optically active amylic alcohol of fermentation. It is distinguished from its isomerides by the power which it has of rotating a ray of polarised light, and in a direction (to the right) opposite to that in which the parent alcohol diverts the ray. It has a slightly lower boiling-point and specific gravity than the acid obtained from the inactive alcohol, and furnishes a non-crystalline baric salt, whereas the former yields a crystalline baric salt; on heating to  $200^\circ$  with a small quantity of sulphuric acid it is rendered optically inactive, but still furnishes a gummy baric salt. An acid having similar properties, excepting that it is optically inactive, may be prepared from the ethylic salt formed on distilling ethylic acetomethethacetate with sodic ethylate (see p. 259); probably therefore the optically active acid is *methethacetic acid*,  $\text{CH}(\text{CH}_3)(\text{C}_2\text{H}_5)\cdot\text{COOH}$ .

*Tertiary Valeric or Trimethacetic Acid*,  $\text{C}(\text{CH}_3)_3\text{CO}(\text{OH})$ .—To obtain this acid the  $\delta$ -iodotetrane prepared by acting on tertiary butylic alcohol (trimethylcarbinol) with hydriodic acid is converted into cyanotetrane by the action of mercuric cyanide:  $\text{C}(\text{CH}_3)_3\text{I} + \text{Hg}(\text{CN})_2 = \text{C}(\text{CH}_3)_3\text{CN} + \text{HgICN}$ , which is then heated with water and hydrochloric

acid. Trimethacetic acid is a white crystalline body, slightly soluble in water ; it melts at  $34^{\circ}$ – $35^{\circ}$  and boils at  $161^{\circ}$ .

It will be noticed that the relation in boiling-point and specific gravity between the isomeric butyric and valeric acids is of the same nature as that which obtains between the isomeric paraffins and isomeric alcohols of the ethylic series.

*Palmitic Acid*,  $C_{15}H_{31}CO(OH)$ .—This acid is a constituent in the form of an ethereal salt of nearly all vegetable and animal fats ; thus palm oil consists in the main of glyceric palmitate, and spermaceti of cetylic palmitate. These ethereal salts are readily decomposed by caustic alkalies with formation of an alcohol and a metallic palmitate ; on treating the latter with a mineral acid, crude palmitic acid is obtained, which may be purified by recrystallisation from alcohol. Palmitic acid is a colourless, odourless, and tasteless solid, insoluble in water ; it melts at  $62^{\circ}$ , but cannot be distilled unchanged.

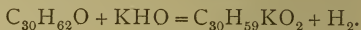
*Stearic Acid*,  $C_{17}H_{35}CO(OH)$ , is present as glyceric stearate (stearin) in most fats, but is especially abundant in beef and mutton suet. It is always obtained admixed with more or less palmitic acid ; to separate it, the mixture is dissolved in hot alcohol and an alcoholic solution of magnesian acetate added ; the magnesian salt which crystallises out consists chiefly of magnesian stearate, which is then decomposed by hydrochloric acid, and the separated stearic acid again similarly treated, and finally repeatedly recrystallised from alcohol until it exhibits a constant melting-point ( $69^{\circ}$ – $70^{\circ}$ ). Like palmitic acid, it is a white crystalline substance, insoluble in water.

*Cerotic Acid*,  $C_{26}H_{53}CO(OH)$ , is the main constituent of the portion of common beeswax soluble in boiling alcohol ; as cerylic cerotate it is almost the sole constituent of Chinese wax. Cerotic acid has been obtained by oxidising solid paraffin with potassic dichromate and sulphuric acid mixture. It crystallises in white grains melting at  $78^{\circ}$  ; it may be distilled unchanged.

By distilling a mixture of baric acetate and baric palmitate or stearate, corresponding ketones (page 323) are obtained, viz.  $C_{15}H_{31}\cdot CO\cdot CH_3$  and  $C_{17}H_{35}\cdot CO\cdot CH_2$  ; on oxidation, these latter are respectively converted into *pentadecylic* and *margaric acid*,  $C_{11}H_{29}\cdot COOH$  and  $C_{16}H_{33}\cdot COOH$ .



*Melissic Acid*,  $C_{29}H_{59}CO(OH)$ , is obtained by oxidising melissic alcohol (page 161) by fusing it with potassic hydrate :



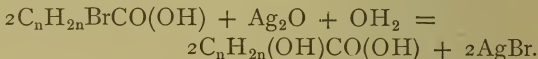
It closely resembles cerotic acid, but melts at  $88^{\circ}$ - $89^{\circ}$ .

### $C_nH_{2n}(OH)CO(OH)$ OR LACTIC SERIES OF MONOBASIC ACIDS.

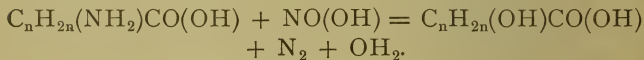
The acids of this secondary series are the mono-hydroxyl derivatives of the acids of the acetic series, to which they bear the same relation that the monohydric alcohols of the ethylic series bear to the paraffins ; hence they are termed monobasic dihydric acids :



*Formation.*—1. By the action of argentic oxide and water (argentic hydrate?) on the monochlorinated, monobrominated, or moniodated acids of the acetic series :

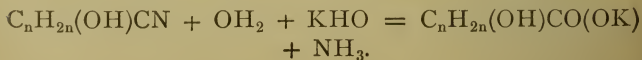


2. By the action of nitrous acid on the monamido-derivatives of the acids of the acetic series (p. 265) :

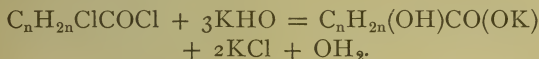


3. By oxidation of the glycols by dilute nitric acid, argentic oxide, or in contact with platinum black.

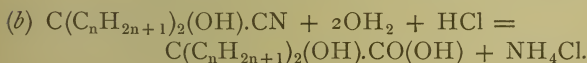
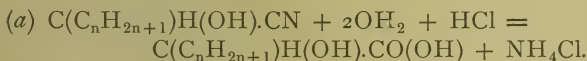
4. As potassic salts by boiling the cyanides obtained by the action of potassic cyanide on the chlorhydrins of the glycols (formed either by the union of the olefines with hypochlorous acid (p. 96), or by the action of hydrochloric acid on the glycols (p. 174), with potassic hydrate solution :



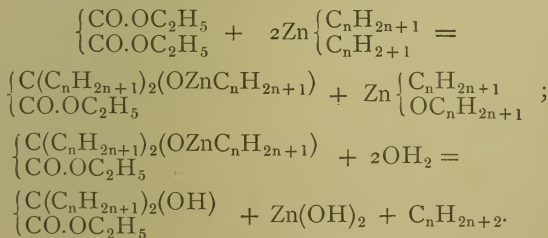
5. As potassic salts, by the action of potassic hydrate solution on the acid chlorides of the monochlorinated acids of the acetic series formed by the union of the olefines and carbonic oxychloride (p. 56) :



6. By digesting the cyanides formed by the union of (a) the aldehydes of the acetic series and hydrocyanic acid (p. 220), and (b) the ketones of the form  $\text{CO}(\text{C}_n\text{H}_{2n+1})_2$  and hydrocyanic acid, with hydrochloric acid solution :



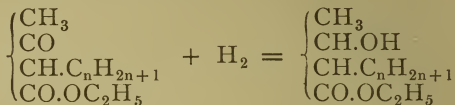
7. As ethylic salts by the action of the zinc organo-metallic compounds<sup>1</sup> on ethylic oxalate, and subsequent treatment of the product with water (Frankland and Duppa) :



8. As ethylic salts by the action of nascent hydrogen on the compounds of the form  $\left\{ \begin{array}{l} \text{CH}(\text{C}_n\text{H}_{2n+1})(\text{CH}_3\text{CO}) \\ \text{CO.OC}_2\text{H}_5 \end{array} \right\}$  ob-

<sup>1</sup> The zinc organo-metallic compound may be prepared *in situ* ; i.e., the reaction may be effected simply by employing a mixture of ethylic oxalate, zinc, and a moniodoparaffin.

tained by acting upon the compound  $C_6H_9NaO_3$  (p. 257) with the moniodoparaffins :



*Mode of classifying the Acids of the Lactic Series.*—The isomeric acids may be arranged in a number of series according to the methods employed in their formation and their behaviour on oxidation and with various reagents. Thus we may distinguish—

I. PRIMARY ACIDS,  $\begin{Bmatrix} C(C_nH_{2n+1})H.OH \\ CO.OH \end{Bmatrix}$ , which appear to be

always formed by the application of method 1 to the mono-haloid derivatives produced by acting upon the *primary acids* of the acetic series with chlorine or bromine, and are also produced on oxidation of the glycols :  $C(C_nH_{2n+1})H(OH).CH_2(OH)$ , and from the aldehydes of the acetic series by method 6.

2. SECONDARY ACIDS,  $\begin{Bmatrix} C(C_nH_{2n+1})_2.OH \\ CO.OH \end{Bmatrix}$ , which apparently

are always produced by the application of method 1 to the mono-haloid derivatives obtained by acting upon the *secondary acids* of the acetic series with chlorine or bromine, and are also formed from the ketones by method 6, and from ethylic oxalate by method 7.

3. PRIMARY OLEFINE ACIDS,  $C_nH_{2n} \begin{Bmatrix} CH_2.OH \\ CO.OH \end{Bmatrix}$ , formed by oxidation of the primary glycols.

4. SECONDARY OLEFINE ACIDS,  $C_nH_{2n} \begin{Bmatrix} C(C_nH_{2n+1})H.OH \\ CO.OH \end{Bmatrix}$ , formed by method 8.

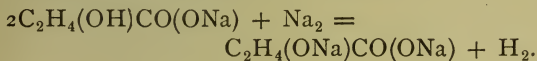
5. TERTIARY OLEFINE ACIDS,  $C_nH_{2n} \begin{Bmatrix} C(C_nH_{2n+1})_2.OH \\ CO.OH \end{Bmatrix}$ .

Acids of this series have not as yet been produced.

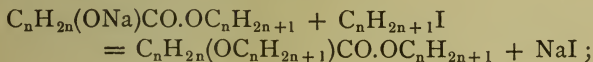
Each of these series may include normal and iso-acids.

*Properties.*—The acids of the lactic series furnish metallic salts of the composition  $C_nH_{2n}(OH)CO.OM'$ ,  $(C_nH_{2n}(OH)CO_2)_2M''$ , &c., when acted upon by metallic

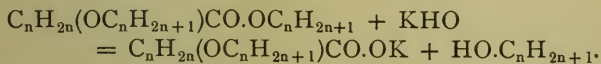
carbonates, and they furnish corresponding ethereal salts ( $C_nH_{2n}(OH)CO.OC_nH_{2n+1}$ , &c.), when acted upon by the alcohols. But it is also possible to replace a second unit of hydrogen by metals ; thus, by carefully fusing sodic lactate with sodium, a disodic lactate is produced :



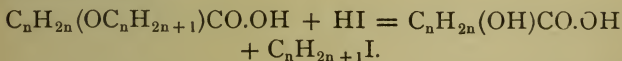
This derivative, however, cannot be dissolved in water unchanged, but is resolved into sodic lactate and sodic hydrate, just in the same manner that sodic ethylate is converted by water into alcohol and sodic hydrate. Similarly, potassium and sodium dissolve with evolution of hydrogen in the ethereal salts of the acids of the lactic series, producing metallic derivatives of the form  $C_nH_{2n}(ONa)CO(OC_nH_{2n+1})$ , which may be converted by the action of the moniodo-paraffins into the ethereal salts of what are appropriately termed *etheric acids* of the lactic series :



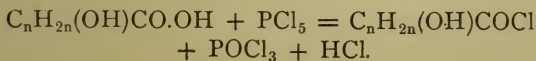
from which the potassic salts of etheric acids are obtained on heating with potassic hydrate solution :



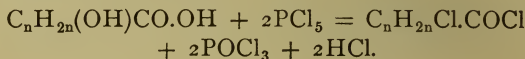
These etheric acids are not decomposed by alkalies, but are converted into acids of the lactic series on heating with hydriodic acid :



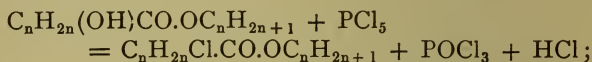
2. By the action of phosphorus pentachloride on the acids of the lactic series, or their metallic salts, the corresponding acid chlorides are formed, thus :



This action takes place either in the cold or on warming gently, but on heating more strongly with an excess of the chloride, the acid chloride of a monochlorinated acid of the acetic series is produced :



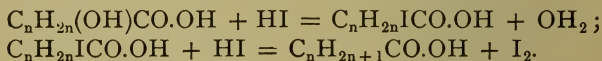
By the action of the haloid phosphorus compounds on the ethereal salts of the acids of the lactic series, the ethereal salts of mono-haloid derivatives of the acids of the acetic series are produced, e.g. :



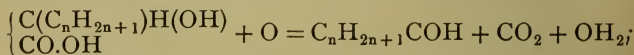
in many cases, however, the product is at once resolved into hydrochloric acid, and the ethereal salt of the corresponding acid of the acrylic series :



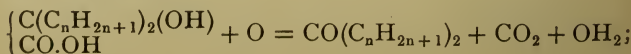
3. By heating the acids of the lactic series with a concentrated aqueous solution of hydriodic acid, they are reduced to the corresponding acids of the acetic series :



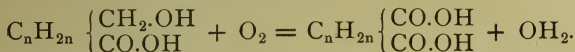
4. The acids of the lactic series are readily oxidised, and furnish characteristic products, but the law of oxidation is not yet fully worked out; the primary acids apparently always furnish an aldehyde, carbonic anhydride, and water :



whilst the secondary acids yield a ketone, carbonic anhydride, and water :



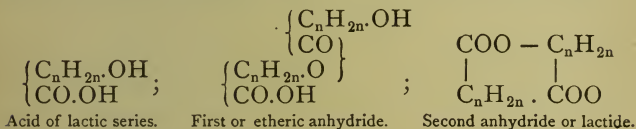
and the primary olefine acids are converted into the corresponding dibasic acids of the succinic series :



5. Several of the acids of the series are converted into the corresponding acids of the acrylic series and water on dry distillation :



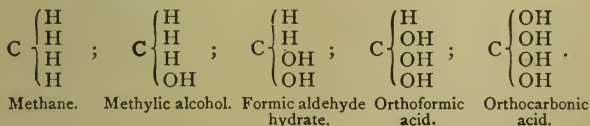
Others yield anhydrides, two of which are formed, thus :



The etheric anhydrides are monobasic acids ; the lactides are indifferent bodies.

CARBONIC ACID,  $H_2CO_3 = CO(OH)_2$ .—This acid is the first term of the lactic series, being the monohydroxyl derivative of formic acid,  $HCO(OH)$ , the first term of the acetic series.<sup>1</sup> It is, however, a dibasic acid. Although

<sup>1</sup> If the oxidation of the alcohols and aldehydes be regarded as the result of double decomposition in the manner previously indicated (pp. 216, 241), carbonic acid, or rather orthocarbonic acid, is the final product of the oxidation of methylic alcohol, the monohydroxyl derivative of methane, thus :

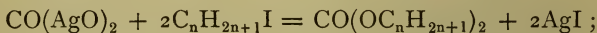


Neither formic aldehyde-hydrate nor orthoformic acid are known as such, both being compounds of exceedingly low stability, but, as already stated, their ethereal derivatives are stable bodies ; similarly, although we have no knowledge of orthocarbonic acid, and only assume its existence on theoretical grounds, an *ethylic orthocarbonate* is known which is a highly

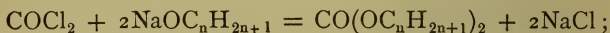


carbonic acid is so unstable that it at once breaks up into carbonic anhydride and water, it furnishes a large number of highly stable metallic and ethereal salts. It is unnecessary to describe in this place the formation of the metallic carbonates.

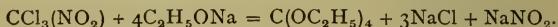
*Ethereal Salts.*—Carbonic anhydride unites with the potassium and sodium derivatives of the alcohols; thus when it is passed into a solution of potassic hydrate in anhydrous alcohol, *potassic ethylic carbonate*,  $\text{CO} \left\{ \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OK} \end{smallmatrix} \right.$ , is produced.<sup>1</sup> The compounds so formed are at once decomposed by water into the corresponding alcohol and hydric potassic (or sodic) carbonate. The normal ethereal salts of carbonic acid are obtained by the action of the mono-haloid hydrocarbon derivatives on argentic carbonate:



by the action of carbonic oxychloride on the sodium derivatives of the alcohols:

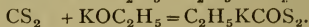
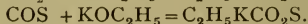
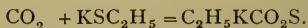


stable compound. It is obtained by the action of sodic ethylate on nitrotrichloromethane (chloropicrin):



Ethylic orthocarbonate is an oily colourless liquid, boiling at  $158^\circ$ – $160^\circ$ .

<sup>1</sup> Similarly, carbonic anhydride unites with the sodium derivatives of the mercaptans, and carbonic oxysulphide and carbonic disulphide unite with the sodium derivatives of the alcohols and mercaptans, thus:



The stability of these compounds increases as the proportion of sulphur contained in them increases; thus the two latter yield the corresponding hydrogen salts,  $\text{C}_2\text{H}_5\cdot\text{HCOS}_2$  and  $\text{C}_2\text{H}_5\cdot\text{HCS}_3$ , in the form of oily liquids on treatment with dilute hydrochloric acid (compare page 58).

and by the action of sodium or potassium on the corresponding ethereal salts of oxalic acid :



They are, with few exceptions, colourless liquids, difficultly soluble in water, which can be distilled unchanged ; in contact with water in the cold they are only slowly decomposed, but on heating are rapidly resolved into the alcohol and carbonic acid.

*Ethylic Carbonate*,  $\text{CO}(\text{OC}_2\text{H}_5)_2$ .—Carbonic oxychloride is absorbed by anhydrous alcohol with formation of hydrochloric acid and *ethylic chlorocarbonate*,  $\text{COCl}(\text{OC}_2\text{H}_5)$ , a mobile colourless liquid, boiling at  $94^\circ$  ; it possesses a suffocating odour and has a most irritating action on the eyes. It is slowly decomposed in contact with water.

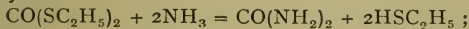
On heating ethylic chlorocarbonate with alcohol it is converted into ethylic carbonate and hydrochloric acid. Ethylic carbonate may also be prepared by the general methods above mentioned ; it is a mobile colourless liquid, of sweet ethereal odour, boiling at  $125^\circ$ . An interesting series of bodies, derived from ethylic carbonate by the gradual substitution of sulphur for oxygen, have been obtained ; such are the following :—

|                                                                                                           | B.-P.       |                                                                                                         | B.-P.       |
|-----------------------------------------------------------------------------------------------------------|-------------|---------------------------------------------------------------------------------------------------------|-------------|
| $\text{CO} \left\{ \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{array} \right.$   | $125^\circ$ |                                                                                                         |             |
| $\text{CO} \left\{ \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{array} \right.$   | $156^\circ$ | $\text{CS} \left\{ \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{array} \right.$ | $161^\circ$ |
| $\text{CO} \left\{ \begin{array}{l} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{array} \right.^2$ | $196^\circ$ | $\text{CS} \left\{ \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{array} \right.$ | $200^\circ$ |
|                                                                                                           |             | $\text{CS} \left\{ \begin{array}{l} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{array} \right.$ | $240^\circ$ |

*Amides of Carbonic Acid*.—Carbonic acid yields both an acid

<sup>1</sup> The probable explanation of this change has been given on p. 261.

<sup>2</sup> This compound, obtained by the action of carbonic oxychloride on sodium-mercaptide, yields carbamide (urea) and mercaptan on decomposition by ammonia :



whereas the isomeric compound, obtained by the action of ethylic

amide (*carbamic acid*) and a normal amide (*carbamide*). On passing dry ammonia gas and carbonic anhydride into anhydrous alcohol, a white crystalline body is obtained, which is the ammoniac salt of carbamic acid,  $\text{CO}(\text{NH}_2)(\text{ONH}_4)$ ; ammoniac carbamate is at once decomposed by acids with formation of carbonic acid and an ammoniac salt. Similarly, carbonic oxy-sulphide and carbonic disulphide combine with ammonia forming the compounds  $\text{CS}(\text{NH}_2)(\text{ONH}_4)$  and  $\text{CS}(\text{NH}_2)(\text{SNH}_4)$ , and corresponding ethereal salts are obtained by the action of ammonia on the ethereal chlorocarbonates,  $\text{COCl}(\text{OC}_n\text{H}_{2n+1})$ , and the ethereal carbonates,  $\text{CO}(\text{OC}_n\text{H}_{2n+1})_2$ , &c. Ethylic carbamate originally received the name *urethane*, which has become generic, all compounds of the form  $\text{CO}(\text{NH}_2)(\text{OR})$  being termed *urethanes*.

**CARBAMIDE (urea),  $\text{CO}(\text{NH}_2)_2$ .**—This compound is one of the chief solid constituents of human urine, hence the name urea, and especial interest attaches to it as it was the first organic compound artificially produced. Urea is obtained in a variety of ways: by the action of ammonia on carbonic oxychloride; by heating ethylic carbonate with ammonia; by heating ammoniac carbamate or ordinary commercial ammoniac carbonate in closed tubes for some hours at  $130^\circ$ – $140^\circ$ ; and by the action of heat on ammoniac cyanate,  $\text{NH}_4\text{CNO}$ . It was by this last method that Woehler first obtained urea. Ammoniac cyanate is prepared by mixing solutions of potassic cyanate and ammoniac sulphate; the solution is then boiled a short time, which suffices to convert the whole of the cyanate into urea. Urea crystallises in long white irregular flattened prisms, very soluble in water; on prolonged boiling with potassic hydrate solution it is resolved into ammonia and potassic carbonate:



Urea combines with acids: thus with hydrochloric acid it forms bromide on the product of the union of carbonic disulphide and potassic ethylate (potassic xanthate), yields ammoniac sulphocyanate, alcohol, and mercaptan:



the compound  $\text{CON}_2\text{H}_4\cdot\text{HCl}$ ; and with nitric acid the compound  $\text{CON}_2\text{H}_4\cdot\text{HNO}_3$ . The latter salt may be employed in the detection of urea: being difficultly soluble in nitric acid, it is at once precipitated on the addition of the concentrated acid to a moderately strong solution of urea, and when viewed under the microscope the precipitate is seen to consist of rhombic or hexagonal plates which are highly characteristic. Urea also combines with metallic oxides: thus, on the addition of mercuric oxide to a solution of urea to which potassic hydrate has previously been added, a white precipitate of the composition  $\text{CON}_2\text{H}_4\cdot 2\text{HgO}$  is produced. A variety of so-called *compound ureas* are known, derived from urea by the introduction of hydrocarbon groups in place of hydrogen (see *Amines*).<sup>1</sup>

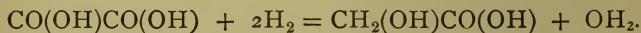
*Isuretine*,  $\text{CON}_2\text{H}_4$ .—This compound, isomeric with ammoniac cyanate and urea, is obtained by digesting a mixture of hydroxylamine,  $\text{NH}_2\cdot\text{OH}$ , and hydrocyanic acid, dissolved in alcohol, at  $40^\circ$ – $50^\circ$ , and subsequently evaporating the solution. It crystallises in large prisms somewhat resembling urea crystals. When boiled with water, it undergoes a complex decomposition, nitrogen and carbonic anhydride being evolved, the solution containing ammonia, *urea*, guanidine, ammoniac formate, and other substances. It forms salts such as the hydrochloride  $\text{CON}_2\text{H}_4\cdot\text{HCl}$  and sulphate  $(\text{CON}_2\text{H}_4)_2\cdot\text{H}_2\text{SO}_4$ ; and also yields

<sup>1</sup> Although urea is very generally regarded as carbamide,  $\text{CO}(\text{NH}_2)_2$ , there is reason to doubt whether this hypothesis affords a correct interpretation of its behaviour: thus, the stability of urea as compared with carbonic and carbamic acids is somewhat remarkable on this assumption; and reactions such as that which occurs when it is evaporated with a solution of argentic nitrate, whereby it is converted into ammoniac nitrate and argentic cyanate, appear to indicate that the nitrogen is not wholly present 'in one form,' as it were. Moreover, very few of the compound ureas resemble urea in their properties, most of them being indifferent substances which do not combine with either acids or bases. The formula  $\text{C}(\text{NH}_2)(\text{NH})(\text{OH})$  is more in accordance with the fact that urea manifests both 'basic' and 'acid' properties, and that it combines with acids always in the proportions required on the assumption that it is a monacid base like ammonia.

precipitates with various metallic salts. It probably has the formula  $\text{CH}(\text{NH})(\text{NH}.\text{OH})$ .

*Sulphocarbamide (Thiourea)*,  $\text{CSN}_2\text{H}_4$ .—This compound bears the same relation to ammoniac sulphocyanate that urea bears to ammoniac cyanate. It is obtained by heating dry ammoniac sulphocyanate at  $170^\circ$  for two to three hours. Thiourea crystallises in white rhombic prisms; it is in all respects the analogue of urea.

GLYCOLLIC or HYDROXYACETIC ACID,  $\text{CH}_2(\text{OH})\text{CO}(\text{OH})$ .—This acid is among the products of the oxidation of alcohol by nitric acid. It is also produced on heating the monohaloid derivatives of acetic acid with water; by the action of nitrous acid on amidoacetic acid (p. 265); by oxidation of glycol (hence the name glycollic acid); and by the action of nascent hydrogen on oxalic acid:



It forms white anhydrous crystals, which melt at  $80^\circ$ ; it is readily oxidised to oxalic acid; by the action of nascent hydrogen it may be reduced to acetic acid.

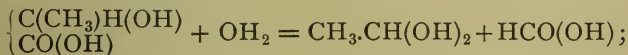
*Thioglycollic Acid*,  $\text{CH}_2(\text{SH})\text{CO}(\text{OH})$ , is produced by heating monochloroacetic acid with a concentrated aqueous solution of potassic sulphhydrate. It is a colourless uncrystallisable oil; on oxidation by dilute nitric acid it is converted into *sulphoacetic acid*,  $\text{CH}_2 \begin{cases} \text{SO}_3\text{H} \\ \text{CO}_2\text{H} \end{cases}$ .

LACTIC ACID.—Three isomeric modifications of this acid are known, namely: ethylidenelactic acid, ethylenelactic acid and sarcolactic acid.

*Fermentation (Ethylidene) Lactic Acid*,  
 $\text{CH}_3.\text{CH}(\text{OH}).\text{CO}(\text{OH})$ .

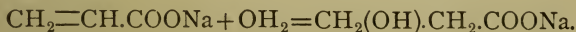
The production of this acid from sugar by fermentation

has been previously described (page 202). It may also be prepared by the action of argentic oxide and water on  $\alpha$ -bromopropionic acid (the first product of the action of bromine on propionic acid); by oxidation of propylene glycol; and from aldehyde by combining it with hydrocyanic acid, and digesting the resulting cyanide with hydrochloric acid solution. It cannot be obtained in the anhydrous condition, so great is the tendency which it exhibits to part with the elements of water and to form anhydrides; thus it has been shown that the syrup which is obtained on exposure of a solution of lactic acid over sulphuric acid in vacuo is not the anhydrous acid, but a mixture of lactic acid with its etheric anhydride and lactide (p. 275). On heating lactic acid for some hours at about  $200^{\circ}$ , it is converted into water and lactic anhydride or *lactide*,  $C_6H_8O_4 = 2C_3H_6O_3 - 2OH_2$ , a white crystalline body, melting at  $124^{\circ}.5$ ; lactide is only very slowly reconverted into lactic acid on digestion with cold water. When heated with sulphuric acid and water at  $140^{\circ}$ – $150^{\circ}$ , lactic acid is resolved into aldehyde and formic acid:



and on oxidation it yields acetic, formic, and carbonic acids. It is readily reduced to propionic acid on heating with a concentrated solution of hydriodic acid; by the action of  $PCl_5$  it is converted into chloropropionic chloride,  $C_2H_4Cl.COCl$ .

*Ethylene-lactic Acid*,  $CH_2(OH).CH_2.CO(OH)$ , is obtained from the monochlorhydrin of glycol,  $CH_2(OH).CH_2Cl$ , by method 4; by method 1 from  $\beta$ -iodopropionic acid (p. 287); and as sodic salt by heating sodic acrylate with a solution of sodic hydrate at  $100^{\circ}$ , thus:





On distillation, it is almost completely resolved into acrylic acid,  $\text{CH}_2=\text{CH}.\text{COOH}$ , and water; hence it has been termed hydracrylic acid.

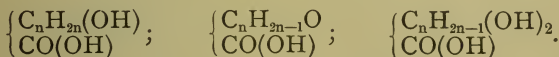
*Sarcolactic or Paralactic acid*.—Flesh juice contains an acid precisely similar in its general chemical behaviour to the ordinary lactic acid produced by fermentation, but distinguished from it by possessing the property of rotating rays of plane polarised light slightly to the right; the zincic salts of the two acids are also different, zincic sarcolactate crystallising on slow evaporation of its aqueous solution in short thick glistening crystals of the composition  $\text{C}_6\text{H}_{10}\text{O}_6\text{Zn}, 2\text{OH}_2$ , whereas zincic lactate forms small colourless prisms of the composition  $\text{C}_6\text{H}_{10}\text{O}_6\text{Zn}, 3\text{OH}_2$ , and is only about one-third as soluble as zincic sarcolactate in cold water. On exposure of a solution of sarcolactic acid over sulphuric acid in vacuo, a mixture of the etheric anhydride and lactide is produced, similar to that obtained in like manner from fermentation lactic acid, but both products from sarcolactic acid are optically active, manifesting considerable lævorotatory power. The lactide produced on heating sarcolactic acid is apparently identical with that from ordinary lactic acid. No satisfactory explanation has hitherto been given of the relation which these two acids bear to each other; and it may be doubted whether any explanation can be given on the hypothesis that isomerides are necessarily bodies of different rational formulæ. Sarcolactic acid probably bears a somewhat similar relation to the ordinary acid that the optically active modifications of tartaric bear to either racemic or mesotartaric acid (page 313).

DIMETHYLHYDROXYACETIC ACID (*dimethoxatic acid*),  $(\text{CH}_3)_2\text{C}(\text{OH}).\text{COOH}$ , is readily prepared by method 7 from ethylic oxalate and zincic methide; it is also produced by oxidation of dimethacetic acid,  $(\text{CH}_3)_2\text{CH}.\text{COOH}$ , by a

solution of potassic permanganate, its formation in this manner affording one of the few instances of the direct substitution of the group OH for H by means of an oxidising agent. It has already been pointed out that this change very probably always takes place, but as a rule the resulting compound at once undergoes further change. Dimethylhydroxyacetic acid is a crystalline substance resembling oxalic acid in appearance ; it boils at about  $212^{\circ}$ , and may be distilled unchanged. On oxidation with a mixture of potassic dichromate and sulphuric acid, it is converted into acetone,  $\text{CO}(\text{CH}_3)_2$ , and carbonic acid.

$\text{C}_n\text{H}_{2n-1}\text{O}.\text{CO}(\text{OH})$  OR PYRUVIC SERIES OF MONOBASIC ACIDS.

The acids of this series are monohydric monobasic acids ; they may be regarded as derived from the acids of the lactic series by the abstraction of two units of hydrogen, and from the acids of the glyoxylic series by the abstraction of the elements of water ; thus :



Acid of lactic series.

Acid of pyruvic series.

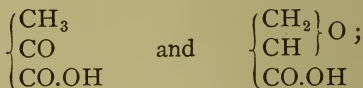
Acid of glyoxylic series.

The following are known :—

|                            |   |   |   |                                        |
|----------------------------|---|---|---|----------------------------------------|
| Glyoxalic acid             | . | . | . | $\text{C}_2\text{H}_2\text{O}_3$       |
| Pyruvic (pyroracemic) acid | . | . | . | $\text{C}_3\text{H}_4\text{O}_3$       |
| Epihydric acid             | . | . | . | $\text{C}_4\text{H}_6\text{O}_3$       |
| Acetopropionic acid        | . | . | . | $\text{C}_5\text{H}_8\text{O}_3$       |
| Convolvulinoleic acid      | . | . | . | $\text{C}_{13}\text{H}_{24}\text{O}_3$ |
| Jalapinoleic acid          | . | . | . | $\text{C}_{16}\text{H}_{30}\text{O}_3$ |
| Ricinoleic acid            | . | . | . | $\text{C}_{18}\text{H}_{34}\text{O}_3$ |

GLYOXALIC ACID,  $C_2H_2O_3 = COH.CO(OH)$ .—See *Glyoxylic Acid* (p. 286).

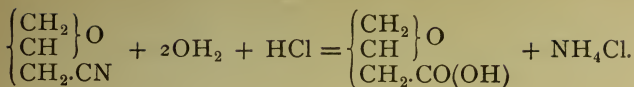
PYRUVIC ACID (*Pyroracemic acid*),  $C_2H_3O.CO(OH)$ , is produced by the dry distillation of racemic or tartaric acid,  $C_4H_6O_6 = C_3H_4O_3 + CO_2 + OH_2$ ; and by dry distillation of glyceric acid. It is a liquid, smelling like acetic acid, soluble in water, and boiling at about  $165^\circ$ , but with partial decomposition. By the action of nascent hydrogen it is converted into fermentation lactic acid; it unites with bromine to form the compound  $C_3H_4Br_2O_3$  (*dibromolactic acid?*). Two formulæ have been proposed for this acid:



but the former appears to be the correct expression, as pyruvic acid may be obtained from the cyanide,  $CH_3.CO.CN$ , produced by the action of argentic cyanide on acetic chloride, by first converting this cyanide into the amide  $CH_3.CO.CONH_2$  by the action of hydrochloric acid of sp. gr. 1.20 at  $0^\circ$ , and then gently heating this amide with a slight excess of hydrochloric acid.

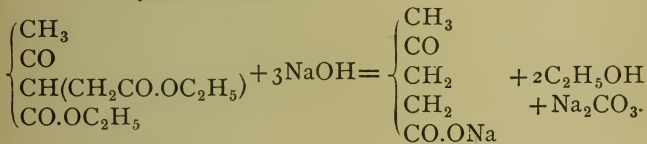
EPIHYDRIC ACID,<sup>1</sup>  $C_4H_6O_3$ , is obtained by heating epicyanhydrin (the product of the action of potassic cyanide on epichlorhydrin, p. 180) with hydrochloric acid solution:

<sup>1</sup> The ethylic acetoacetate,  $\left\{ \begin{array}{l} CH_2(COCH_3) \\ CO.OC_2H_5 \end{array} \right.$ , obtained by Geuther (page 257) is the ethylic salt of an acid isomeric with epihydric acid; and the compounds of the form  $\left\{ \begin{array}{l} CH(C_nH_{2n+1})(COCH_3) \\ CO.OC_2H_5 \end{array} \right.$  and  $\left\{ \begin{array}{l} C(C_nH_{2n+1})_2(COCH_3) \\ CO.OC_2H_5 \end{array} \right.$  obtained by Frankland and Duppa (p. 258) are ethylic salts of homologous acids. These ethylic salts have not hitherto been converted into the corresponding acids, however.



It is a white crystalline acid, melting at  $225^\circ$ ; when heated with hydriodic acid it yields normal butyric acid.

ACETOPROPIONIC ACID,  $\text{C}_5\text{H}_8\text{O}_3$ .—The sodic salt of this acid is produced on boiling the product of the action of ethylic monochloracetate on ethylic acetosodacetate (p. 257), with sodic hydrate solution :



RICINOLEIC ACID,  $\text{C}_{18}\text{H}_{34}\text{O}_3$ .—The glyceric salt of this acid is the essential constituent of castor oil. Ricinoleic acid is a yellow inodorous oil; when cooled below  $0^\circ$ , it solidifies to a granular mass. On dry distillation of castor oil or sodic ricinoleate, a considerable quantity of an heptylic aldehyde (*œnanthol*),  $\text{C}_7\text{H}_{14}\text{O}$ , is obtained, which is convertible by the action of nascent hydrogen into normal primary heptylic alcohol. On heating sodic ricinoleate with an excess of sodic hydrate, secondary octylic alcohol and sodic sebate are obtained :

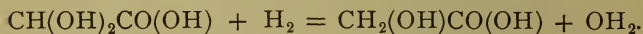


$\text{C}_n\text{H}_{2n-1}(\text{OH})_2$  OR GLYOXYLIC SERIES OF MONOBASIC ACIDS.

Two acids of this series are known: glyoxylic acid,  $\text{C}_2\text{H}_4\text{O}_4$ , and glyceric acid,  $\text{C}_3\text{H}_6\text{O}_4$ . Both are trihydric monobasic acids.

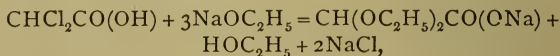
GLYOXYLIC ACID (*dioxyacetic acid*),  $C_2H_4O_4 = CH(OH)_2CO(OH)$ , is amongst the products of the oxidation of alcohol and of glycol by nitric acid; it is also obtained by the action of nascent hydrogen (evolved by zinc and sulphuric acid) on oxalic acid:  $CO(OH)CO(OH) + H_2 = CH(OH)_2CO(OH)$ ; and by boiling the silver salt of dibromacetic acid with water.

Glyoxylic acid crystallises in prisms, very soluble in water; by boiling its calcic salt with lime water, calcic glycollate and oxalate are produced;<sup>1</sup> it dissolves zinc without evolution of hydrogen, zincic glycollate being formed:

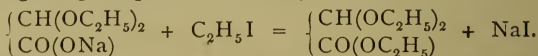


Most of the metallic glyoxylates have the composition indicated by the formula  $C_2H_3M'O_4$ ; thus argentic glyoxylate is  $C_2H_3AgO_4$ , and calcic glyoxylate is  $(C_2H_3O_4)_2Ca$ . But ammonic glyoxylate has the composition  $C_2H(NH_4)O_3$ , and, on this account, Debus, the discoverer of the acid, assigns to it the formula  $C_2H_2O_3 = COHCO(OH)$ , and regards the salts of the form  $C_2H_3M'O_4$  as salts containing water of crystallisation. It appears in the highest degree probable, however, that both acids exist; the relation of the acid  $COHCO(OH)$ , which is appropriately termed *glyoxalic acid*, to glyoxylic acid,  $CH(OH)_2CO(OH)$ , being obviously of the same nature as the relation between aldehyde,  $CH_3COH$ , and aldehyde-hydrate,  $CH_3CH(OH)_2$ , of the existence of which latter compound there can be little doubt, although it cannot be isolated.

The ethylic salt of the etheric acid,  $CH(OC_2H_5)_2CO(OH)$ , derived from glyoxylic acid, is produced by heating dichloroacetic acid with sodic ethylate:



and digesting the product with ethylic iodide:



<sup>1</sup>  $2[CH(OH)_2CO_2]_2Ca + Ca(OH)_2 = [CH_2(OH).CO_2]_2Ca + C_2O_4Ca + OH_2.$

It is a colourless mobile liquid of pleasant fruity odour, which boils at  $199^{\circ}$ ; by the action of ammonia it is converted into the amide  $\text{CH}(\text{OC}_2\text{H}_5)_2\text{CO}(\text{NH}_2)$ , a white crystalline compound.

GLYCERIC ACID (*dioxypropionic acid*),  $\text{C}_3\text{H}_6\text{O}_4 = \text{CH}_2(\text{OH}).\text{CH}(\text{OH}).\text{CO}(\text{OH})$ , is obtained by oxidising glycerin with nitric acid. It is a thick non-crystallising syrup; phosphorus iodide converts it into  $\beta$ -iodopropionic iodide, which on treatment with water yields  $\beta$ -iodopropionic acid,<sup>1</sup>  $\text{CH}_2\text{I}.\text{CH}_2\text{CO}(\text{OH})$ .

$\text{C}_n\text{H}_{2n-1}\text{CO}(\text{OH})$  OR ACRYLIC SERIES OF MONOBASIC ACIDS.

The acids of this series bear the same relation to the acids of the acetic series that the alcohols of the vinylic series bear to the alcohols of the ethylic series. The following are known :—

|                            |   |   |   |                                            |
|----------------------------|---|---|---|--------------------------------------------|
| *Acrylic acid <sup>2</sup> | . | . | . | $\text{C}_2\text{H}_3\text{CO}(\text{OH})$ |
| *Crotonic acid             | . | } | . | $\text{C}_3\text{H}_5\text{CO}(\text{OH})$ |
| *Methacrylic acid          | . |   | . |                                            |
| *Angelic acid              | . | } | . | $\text{C}_4\text{H}_7\text{CO}(\text{OH})$ |
| *Methylcrotonic acid       | . |   | . |                                            |
| *Pyroterebic acid          | . | } | . | $\text{C}_5\text{H}_9\text{CO}(\text{OH})$ |
| *Ethylcrotonic acid        | . |   | . |                                            |
| *Hydrosorbic acid          | . |   | . |                                            |

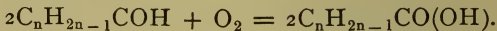
<sup>1</sup>  $\beta$ -Chloro- and bromo-propionic acid are similarly prepared by the action of phosphorus chloride and bromide.  $\alpha$ -Iodopropionic acid,  $\text{CH}_3.\text{CHI}.\text{CO}(\text{OH})$ , is obtained by acting on fermentation lactic acid with phosphorus iodide and subsequently treating the product with water;  $\alpha$ -chloro- and bromo-propionic acid are similarly prepared by the action of phosphorus chloride and bromide, and also by the direct action of chlorine and bromine on propionic acid. By heating  $\alpha$ -bromopropionic acid with bromine it is converted into  $\alpha$ -dibromopropionic acid,  $\text{CH}_3.\text{CBr}_2.\text{CO}(\text{OH})$ . The  $\alpha$ -mono-haloid derivatives of propionic acid are fluid bodies; the  $\beta$ -derivatives are white crystalline compounds.

<sup>2</sup> The acids marked thus \* have been artificially produced; the remainder, of which, with few exceptions, our knowledge is very imperfect, are obtained from natural products.

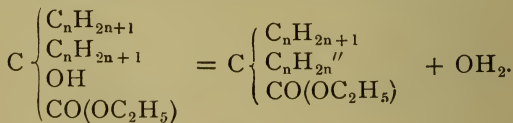


|                  |   |   |   |   |                   |
|------------------|---|---|---|---|-------------------|
| Damaluric acid ? | . | . | . | . | $C_7H_{12}O_2$    |
| Damolic acid ?   | . | . | . | . | $C_{13}H_{24}O_2$ |
| Moringic acid    | } | . | . | . | $C_{15}H_{28}O_2$ |
| Cimicic acid     |   |   |   |   |                   |
| Physetoleic acid | } | . | . | . | $C_{16}H_{30}O_2$ |
| Hypogæic acid    |   |   |   |   |                   |
| Gaïdic acid      |   |   |   |   |                   |
| Oleic acid       | } | . | . | . | $C_{18}H_{34}O_2$ |
| Elaïdic acid     |   |   |   |   |                   |
| Doeglic acid     | . | . | . | . | $C_{19}H_{36}O_2$ |
| Brassic acid     | } | . | . | . | $C_{22}H_{42}O_2$ |
| Erucic acid      |   |   |   |   |                   |

*Formation.*—1. By oxidation of the aldehydes of the acrylic series :



2. By dehydration of certain of the acids of the lactic series. Frankland and Duppa have shown that the ethylic salts of the secondary acids of the lactic series produced by the action of the zinc organo-metallic compounds on ethylic oxalate (p. 271), yield the ethylic salts of the corresponding acids of the acrylic series on distillation with phosphoric anhydride or phosphorus terchloride :

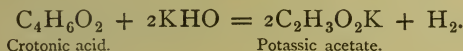
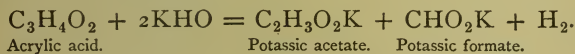


The ethylic salt is saponified in the usual manner with potassic hydrate, and the acrylic acid set free from the potassic salt by the addition of a mineral acid.

*Classification.*—The known acids of the acrylic series are either primary or secondary acids of the following form :



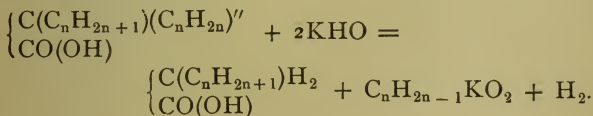
*Properties.*—The acids of the acrylic series are monobasic acids, inasmuch as they furnish metallic salts of the composition  $C_nH_{2n-1}CO_2M$ ,<sup>'</sup>  $(C_nH_{2n-1}CO_2)_2M$ ,<sup>''</sup> &c., and corresponding ethereal salts. They combine with the haloid acids and halogens to form haloid substitution-derivatives of the acids of the acetic series. Most characteristic of these acids, however, is the fact that on fusion with potassic hydrate they furnish the potassic salts of two acids of the acetic series ; thus :



This decomposition is effected in a perfectly definite and regular manner, and appears always to consist in the removal of the  $C_nH_{2n}$  group, and its replacement by  $H_2$ , the  $C_nH_{2n}$  group being separately oxidised to the corresponding acid of the acetic series. Thus the primary acids always furnish potassic acetate as one of the products :<sup>1</sup>



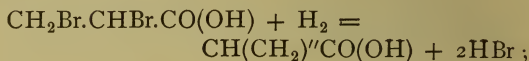
whereas the secondary acids appear to yield the potassic salt of a primary acid of the acetic series homologous with acetic acid as constant product :



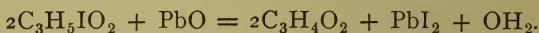
ACRYLIC ACID,  $C_3H_4O_2 = CH(CH_2)''CO(OH)$ .—This acid is the first term of the series. It is obtained 1. by oxidation of acrolein with moist argentic oxide ; 2. by the

<sup>1</sup> The acids of the acrylic series derived from natural products invariably yield potassic acetate as one of the products.

action of nascent hydrogen on  $\beta$ -dibromopropionic acid (produced by oxidising dibromopropylic alcohol, the product of the union of allylic alcohol and bromine, by nitric acid) :



3. by distilling  $\beta$ -iodopropionic acid with plumbic oxide :

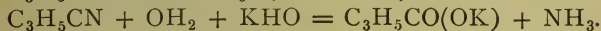
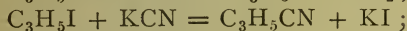
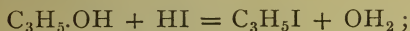


Acrylic acid is a colourless liquid, possessing a penetrating, slightly empyreumatic odour ; it is said that it becomes crystalline when cooled to below  $7^\circ$ . It boils at about  $140^\circ$ .<sup>1</sup> With the exception of the silver salt, all the metallic salts of acrylic acid are very soluble in water. Various ethereal salts of acrylic acid are known, obtained not from the acid itself, but by the action of nascent hydrogen on the ethereal salts of  $\beta$ -dibromopropionic acid. By the action of sodium amalgam on an aqueous solution of acrylic acid, propionic acid is produced ; but the hydrogen evolved by the action of acids on zinc is not able to effect the conversion of acrylic into propionic acid.

**CROTONIC ACID**,  $\text{CH}(\text{CH}.\text{CH}_3)''\text{CO}(\text{OH})$ .—This name was originally assigned to an acid, said to have the composition  $\text{C}_4\text{H}_6\text{O}_2$ , obtained from croton oil, but recent experiments tend to throw doubt on the existence of such an acid in that drug. Crotonic acid is obtained 1. on oxidation of crotonic aldehyde by moist argentic oxide ; 2. on

<sup>1</sup> It is noteworthy that the boiling-points of allylic alcohol, acrylic acid, and the ethereal salts of acrylic acid are identical, or nearly so, with the boiling-points of the isologous bodies propylic alcohol, propionic acid, &c. Thus, allylic and propylic alcohols boil at about  $96^\circ$  ; acrylic and propionic acids at about  $140^\circ$  ; ethylic acrylate and propionate at about  $101^\circ$  ; and allylic acrylate and propylic propionate at about  $124^\circ$ .

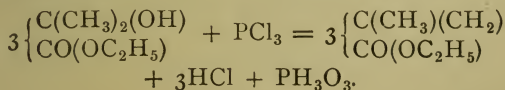
dry distillation of  $\beta$ -oxybutyric acid (p. 257); and 3. as potassic salt from allylic alcohol by the following series of reactions:



It is a white crystalline substance, which melts at  $72^\circ$ , and boils at  $181^\circ$ ; on fusion with potassic hydrate it yields potassic acetate and hydrogen.

On account of the production of crotonic acid from allylic alcohol, which is generally admitted to be correctly represented by the formula  $\text{CH}(\text{CH}_2)''\cdot\text{CH}_2(\text{OH})$ , it has been usual to assign to it the formula  $\text{CH}(\text{CH}_2)''\cdot\text{CH}_2\text{CO}(\text{OH})$ ; but Kekulé has pointed out that a simple explanation of the formation of crotonic acid from acetaldehyde (p. 227), and of its behaviour on oxidation, is alone afforded by the assumption of the formula  $\text{CH}(\text{CH}\cdot\text{CH}_3)''\text{CO}(\text{OH})$ , and he has succeeded apparently in proving the correctness of his view. A compound represented by the formula  $\text{CH}(\text{CH}_2)''\text{CH}_2\text{R}'$ , Kekulé considers, cannot furnish acetic acid on oxidation, and as a matter of fact it is found that neither allylic alcohol nor allylic iodide yield that acid on oxidation; the allylic cyanide obtained from the latter by double decomposition with potassic cyanide, however, at once furnishes acetic acid on oxidation, hence the conclusion that during the formation of this body a change occurs of such a nature that instead of a compound of the form  $\text{CH}(\text{CH}_2)''\text{CH}_2(\text{CN})$  being produced, an isomeric compound of the form  $\text{CH}(\text{CH}\cdot\text{CH}_3)''(\text{CN})$  results, which gives rise to the acid  $\text{CH}(\text{CH}\cdot\text{CH}_3)\text{CO}(\text{OH})$ .

METHACRYLIC ACID,  $\text{C}(\text{CH}_3)(\text{CH}_2)''\text{CO}(\text{OH})$ , the isomere of crotonic acid, is obtained (as ethylic salt) on distilling ethylic dimethoxalate with phosphorus terchloride:



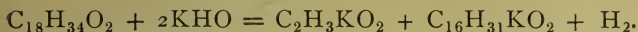
Methacrylic acid is a colourless oily liquid ; on fusion with potassic hydrate it yields potassic propionate, potassic formate, and hydrogen.

OLEIC ACID,  $C_{18}H_{34}O_2=CH(C_{16}H_{32})''CO(OH)$ , is present as glyceric oleate (*olein*),  $C_3H_5(C_{18}H_{33}O_2)_3$ , in most natural fats and fixed non-drying oils.<sup>1</sup>

To obtain the pure acid, olive or almond oil is saponified with potassic hydrate, the resulting soap is decomposed by tartaric acid, the mixture of oleic and stearic acids thus obtained is converted into plumbic salts by digestion with plumbic oxide, and the mixed salts are shaken up with ether, which extracts the oleate, leaving the stearate undissolved ; the oleic acid is then liberated by the addition of hydrochloric acid, the ethereal solution is decanted from the watery liquid, the ether distilled off, and the crude acid which remains converted into baric salt, which is recrystallised from alcohol, then decomposed by tartaric acid, and the separated acid recrystallised from alcohol until of constant melting-point.

Oleic acid crystallises in white needles, which melt at  $14^\circ$  ; it is insoluble in water. In the solid state it slowly absorbs oxygen, but in the liquid state it is rapidly oxidised on exposure to the air. On fusion with potassic hydrate it yields potassic acetate and potassic palmitate :

<sup>1</sup> The natural fixed oils are divided into *non-drying* and *drying oils*. When exposed to the air the latter thicken, owing to the absorption of oxygen ; the former are also gradually altered, though in a different manner. The non-drying oils contain glyceric oleate, or glyceric salts of acids homologous with oleic acid. Owing to partial decomposition of these salts, induced apparently by associated foreign matters which act as ferments, the oils become rancid on keeping ; by washing with a weak alkaline solution they may be freed from the products of decomposition and restored to their original state ; but this is not the case with the drying oils, which contain glyceric salts of acids of some other series than the oleic. Thus linseed, poppy, and hemp oil contain the glyceric salt of an acid termed *linoleic* acid, which is said to have the composition  $C_{18}H_{28}O_2$ .



When nitric peroxide is passed into liquid oleic acid, it is rapidly converted into a solid isomeric compound, *elaïdic acid*. Elaïdic acid is a crystalline body which melts at about  $44^\circ$ . It is a far more stable body than oleic acid : thus it may be distilled unchanged, whereas oleic acid is decomposed on distillation, and even in the liquid state it only slowly absorbs oxygen. On fusion with potassic hydrate, elaïdic acid furnishes the same products as oleic acid.

*Brassic Acid*,  $\text{C}_{22}\text{H}_{42}\text{O}_2$ , is obtained from colza oil (the oil expressed from the seeds of various species of *Brassica*) in the same way that oleic acid is obtained from olive oil.

$\text{C}_n\text{H}_{2n-3}\text{CO}(\text{OH})$  OR SORBIC SERIES OF MONOBASIC ACIDS.

The following are known :

|                      |                                                  |          |             |
|----------------------|--------------------------------------------------|----------|-------------|
| Tetroleic acid . . . | $\text{C}_3\text{H}_3\text{CO}(\text{OH})$       | fuses at | $76^\circ$  |
| Sorbic acid . . .    | $\text{C}_5\text{H}_7\text{CO}(\text{OH})$       | „        | $134^\circ$ |
| Stearolic acid . . . | $\text{C}_{17}\text{H}_{31}\text{CO}(\text{OH})$ | „        | $48^\circ$  |

*Tetroleic Acid* is produced by the action of an alcoholic solution of potassic hydrate on chlorocrotonic acid,  $\text{C}_3\text{H}_4\text{ClCO}(\text{OH})$ .

*Sorbic Acid* is a crystalline acid, present in mountain-ash berries. Nascent hydrogen (evolved by sodium amalgam and water) converts it into the corresponding acid of the acrylic series, hydrosorbic acid,  $\text{C}_5\text{H}_9\text{CO}(\text{OH})$ ; it unites with bromine to form the compound  $\text{C}_6\text{H}_8\text{Br}_4\text{O}_4$ .

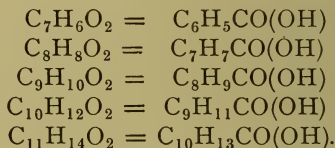
*Stearolic Acid* is obtained by heating bromoleic acid with an alcoholic solution of potassic hydrate. It is not affected by nascent hydrogen, but combines with bromine in two proportions to form the compounds  $\text{C}_{18}\text{H}_{32}\text{Br}_2\text{O}_2$ , and  $\text{C}_{18}\text{H}_{32}\text{Br}_4\text{O}_2$ . On fusion with potassic hydrate it is converted into the potassic salt of an acid of the composition



$C_{16}H_{30}O_2$ , which, by the continued action of potassic hydrate, is converted into the potassic salt of myristic acid,  $C_{14}H_{28}O_2$ —one of the higher homologues of acetic acid.

$C_nH_{2n-7}CO(OH)$  OR BENZOIC SERIES OF MONOBASIC ACIDS.

This series<sup>1</sup> comprises terms of the following composition :



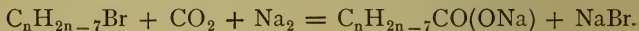
Each of these, however, excepting the first, includes 'a number of isomeric and metameric modifications.

*Formation.*—I. By oxidation of the hydrocarbons of the  $C_nH_{2n-6}$  series (p. 116).

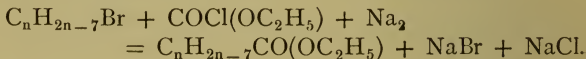
2. By oxidation of the alcohols of the benzylic series.

3. By oxidation of the aldehydes of the benzoic series.

4. As sodic salts by the simultaneous action of sodium and carbonic anhydride on the monobromo-derivatives<sup>2</sup> of the hydrocarbons of the  $C_nH_{2n-6}$  series :



5. As ethylic salts by the action of sodium amalgam on a mixture of a monobromo-derivative<sup>2</sup> of a hydrocarbon of the  $C_nH_{2n-6}$  series, and ethylic chlorocarbonate :

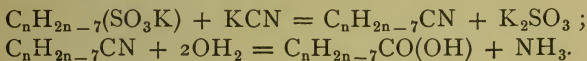


6. By distilling a mixture of potassic cyanide and the

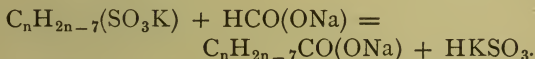
<sup>1</sup> It is also frequently termed the aromatic series.

<sup>2</sup> Hitherto the bromo-derivatives produced by the action of bromine on the cold hydrocarbons have alone been employed.

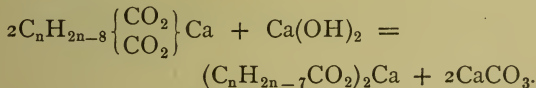
potassic salt of a monosulphonic acid produced by the action of sulphuric acid on a hydrocarbon of the  $C_nH_{2n-6}$  series, and decomposing the resulting cyanide by potassic hydrate solution :



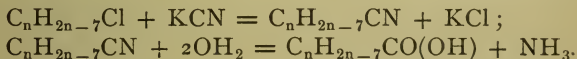
7. By fusing a mixture of sodic formate and the potassic salt of a monosulphonic acid, derived from a hydrocarbon of the  $C_nH_{2n-6}$  series :



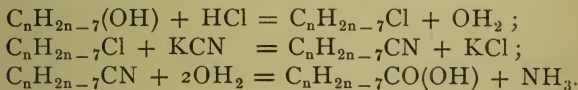
8. By heating a mixture of the calcic salt of a dibasic acid of the phthalic or  $C_nH_{2n-8}(CO.OH)_2$  series, and an equivalent quantity of calcic hydrate at  $300^\circ$ – $400^\circ$  for several hours :



9. From the monochloro- or monobromo-derivatives of the hydrocarbons of the  $C_nH_{2n-6}$  series, produced by the action of chlorine or bromine on the heated hydrocarbons :



10. From the alcohols of the benzylic series, thus :



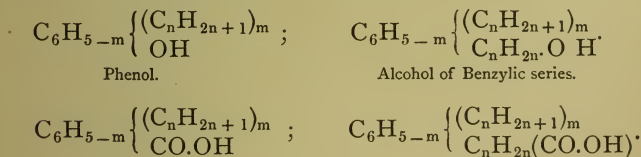
By the aid of these various reactions the following acids of the benzoic series have been produced :—

|                   |                                                                                                                                                                                                 |                                                                                                                                                                  |                                           |
|-------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| $C_7H_6O_2$       | Benzoic acid                                                                                                                                                                                    | $C_6H_5CO(OH)$                                                                                                                                                   | M.-P.<br>121°                             |
| $C_8H_8O_2$       | Paratoluic acid <sup>1</sup><br>Metatoluic acid <sup>2</sup><br>Orthotoluic acid <sup>3</sup><br>Alphatoluic acid <sup>4</sup>                                                                  | $C_6H_4(CH_3)CO(OH)$<br>"<br>"<br>$C_6H_5CH_2CO(OH)$                                                                                                             | 176°<br>109-110<br>102<br>76              |
| $C_9H_{10}O_2$    | Mesitylenic acid <sup>5</sup><br>Paraxylic acid <sup>6</sup><br>Xylic acid <sup>7</sup><br>Ethylbenzoic acid <sup>8</sup><br>Hydrocinnamic acid <sup>9</sup> }<br>Alphaxylic acid <sup>10</sup> | $C_6H_3(CH_3)_2CO(OH)$<br>"<br>"<br>$C_6H_4(C_2H_5)CO(OH)$<br>$C_6H_5CH_2CH_2CO(OH)$<br>$C_6H_4 \left\{ \begin{array}{l} CH_3 \\ CH_2CO(OH) \end{array} \right.$ | 166°<br>163<br>120<br>110-111<br>47<br>42 |
| $C_{10}H_{12}O_2$ | Cumylic acid <sup>11</sup><br>Cumic acid <sup>12</sup>                                                                                                                                          | $C_6H_2(CH_3)_3CO(OH)$<br>$C_6H_4(C_3H_7)CO(OH)$                                                                                                                 | 149-150<br>92                             |
| $C_{11}H_{14}O_2$ | Homocumic acid <sup>13</sup>                                                                                                                                                                    | $C_6H_4 \left\{ \begin{array}{l} C_3H_7 \\ CH_2CO(OH) \end{array} \right.$                                                                                       | 52°                                       |

<sup>1</sup> Obtained by oxidation of paraxylene; yields terephthalic acid on oxidation. <sup>2</sup> Prepared by method 8 from uvitic acid,  $C_6H_3(CH_3)(CO.OH)_2$ , and by the action of nascent hydrogen on the bromotoluic acid formed by oxidising monobromometaxylene; yields isophthalic acid on oxidation. <sup>3</sup> The mixture of toluenepara- and tolueneortho-sulphonic acid, obtained on treating toluene with concentrated sulphuric acid, yields by method 6 a mixture of para- and ortho-toluic acid, which may be separated by fractional crystallisation of the calcic salts; orthotoluic acid yields phthalic acid on oxidation. <sup>4</sup> Prepared from toluene by method 9, and from benzylic alcohol by method 10; yields benzoic acid on oxidation. <sup>5</sup> Obtained by oxidation of mesitylene,  $C_6H_3(CH_3)_3$ ; yields mesidic (uvitic) acid,  $C_6H_3(CH_3)(CO.OH)_2$ , and mesitic acid,  $C_6H_3(CO.OH)_3$ , on oxidation. <sup>6</sup> Obtained together with xylic acid <sup>7</sup> on oxidation of pseudocumene,  $C_6H_3(CH_3)_3$ ; both paraxylic and xylic acid yield xylidic acid,  $C_6H_3(CH_3)(CO.OH)_2$  on oxidation.

*Properties.*—When acted upon by various reagents, the acids of the benzoic series, as a rule, furnish substitution-derivatives, and yield additive compounds only in a certain very limited number of cases; they thus resemble the acids of the acetic series, and differ from the acids of intermediate series in somewhat the same way that the hydrocarbons of the benzene series resemble the paraffins and differ from the hydrocarbons of intermediate series. By the action of the halogens, nitric acid, &c., on the acids of the benzoic series, a multitude of well-characterised crystalline substitution-derivatives are obtained, among which occur numerous instances of isomerism.

*Behaviour on Oxidation.*—The acids tabulated above belong to two metameric series, the relation between which is of the same nature as that which obtains between the phenols and the alcohols of the benzylic series, as will be evident on inspection of the following general formulæ:

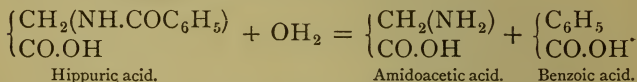


The acids of the series  $\text{C}_6\text{H}_5 - m \left\{ \begin{array}{c} (\text{C}_n\text{H}_{2n+1})_m \\ \text{CO.OH} \end{array} \right.$  are ultimately converted, on oxidation, either into acids of higher basicity of the form  $\text{C}_6\text{H}_5 - m(\text{CO.OH})_{m+1}$ , i.e. into acids containing the same number of units of carbon; or are entirely de-

<sup>8</sup> Prepared by oxidising diethylbenzene with nitric acid; yields terephthalic acid on oxidation. <sup>9</sup> Produced by the union of cinnamic acid and hydrogen; yields benzoic acid on oxidation. <sup>10</sup> Prepared by method 9 from the monochloroxylylene formed by the action of chlorine on boiling xylene; yields benzoic acid on oxidation. <sup>11</sup> Produced by oxidation of tetramethylbenzene (durene). <sup>12</sup> Prepared by oxidation of cumic aldehyde from Roman cumic-oil. <sup>13</sup> Prepared by method 10 from cumic alcohol.

composed. The acids of the series<sup>1</sup>  $C_6H_{5-m} \left\{ \begin{matrix} (C_nH_{2n+1})_m \\ C_nH_{2n}(CO.OH) \end{matrix} \right.$  either yield acids of the form  $C_6H_{5-m}(CO.OH)_{m+1}$ , the  $C_nH_{2n}(CO.OH)$  group being oxidised to  $CO.OH$ ; or they are entirely decomposed.<sup>2</sup>

BENZOIC ACID,  $C_7H_6O_2 = C_6H_5CO(OH)$ , is present in various gums and balsams, and is especially abundant in gum benzoin, the dried exudation from the bark of *Styrax benzoin*—a tree growing in Sumatra, Java, and Borneo. It may be produced by all of the general methods of formation (p. 294); also by oxidation of a mixture of benzene and formic acid (p. 115), and by boiling hippuric acid (*benz-amido-acetic acid*) with hydrochloric acid :



Benzoic acid may be obtained by sublimation in beautiful feathery crystals ; when prepared from gum-benzoin it has a fragrant odour, due to the presence of traces of a volatile oil ; the pure acid is inodorous when cold. Benzoic acid melts at  $121^\circ$ , and boils at about  $239^\circ$  ; it dissolves readily in alcohol and in boiling water, but difficultly in cold water. When acted upon by very concentrated nitric acid, or a mixture of potassic nitrate and sulphuric acid, it is converted into a mixture of *para*-, *meta*-, and *ortho*-nitrobenzoic acid,  $C_6H_4(NO_2)CO(OH)$ ; the first of these isomeric acids is the main product. One of these acids, i.e. *paranitrobenzoic acid*,<sup>3</sup> is produced by oxidising crystalline nitrotoluene (p. 125).

<sup>1</sup> Alphetolucic, hydrocinnamic, alphaxylic, and homocumic acids are members of the series  $C_6H_{5-m} \left\{ \begin{matrix} (C_nH_{2n+1})_m \\ C_nH_{2n}(CO.OH) \end{matrix} \right.$  ; the remaining acids included in the table (p. 296) are members of the metameric series.

<sup>2</sup> Probably in those cases in which the acid is entirely decomposed, the corresponding acid of the  $C_6H_{5-m}(CO.OH)_{m+1}$  series is first formed, but at once further oxidised (see *Phthalic Acid*, p. 319).

<sup>3</sup> The isomeric di-derivatives of benzene are classed in three groups according as they are either derived from, or are convertible into, or

Orthonitrobenzoic acid melts at  $145^{\circ}$ ; metanitrobenzoic acid at  $140^{\circ}$ ; paranitrobenzoic acid at about  $240^{\circ}$ . Each of these acids yields on reduction the corresponding *amidobenzoic acid*,  $C_6H_4(NH_2)CO(OH)$ . These amidobenzoic acids not only form metallic salts in the ordinary manner, but are also capable of combining with the mineral acids to form salts, such as amidobenzoic nitrate,  $C_6H_4(NH_2.HNO_3)CO(OH)$ , &c. This behaviour is characteristic of the amido-acids generally.

Bromine has no action on benzoic acid in the cold, but when heated together they form *metabromobenzoic acid*,  $C_6H_4BrCO(OH)$ ; by prolonged heating with bromine and water, benzoic acid is finally converted into *pentabromobenzoic acid*,  $C_6Br_5CO(OH)$ . On distillation with phosphorus pentachloride, benzoic acid yields *benzoic chloride* (benzoyl chloride),  $C_6H_5COCl$ , as a mobile colourless liquid boiling at  $196^{\circ}$ , which is slowly decomposed by cold water, and reconverted into benzoic acid. By the action of nascent hydrogen (evolved by sodium amalgam) benzoic acid is converted into *hydrobenzoic acid*,  $C_6H_9CO(OH)$ , a crystalline, highly unstable acid, which is gradually reconverted by oxidation into benzoic acid when recrystallised in contact with atmospheric oxygen.

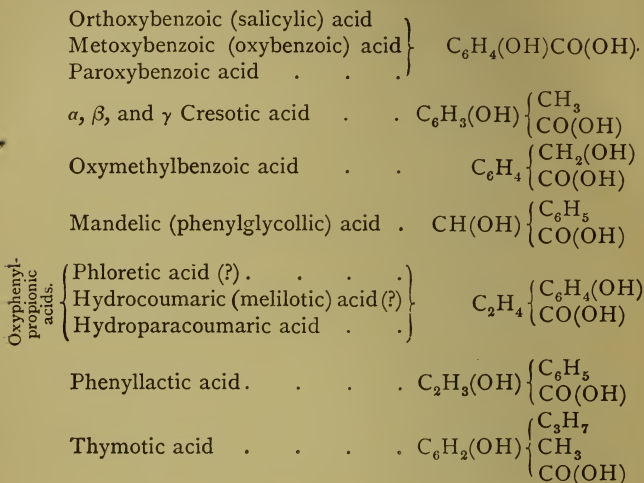
$C_nH_{2n-8}(OH)CO(OH)$  OR OXYBENZOIC (SALICYLIC) SERIES  
OF MONOBASIC ACIDS.

The acids of this series are dihydric monobasic acids, and bear the same relation to the corresponding acids of the

may be more or less directly referred to, either of the three isomeric benzene-dicarboxylic acids: *phthalic acid*, *isophthalic acid*, and *terephthalic acid*; those which are referable to terephthalic acid being termed *para*-derivatives, those referable to isophthalic acid *meta*-derivatives, and those referable to phthalic acid *ortho*-derivatives. The members of these three series are distinguished by differences in crystalline form, melting-point, solubility, &c. The student will find a detailed account of the views which the majority of chemists at present entertain with regard to these isomeric compounds in the articles: Aromatic Series; Benzene, Homologues of; Benzoic Acid; in the Supplements to Watts's 'Dictionary of Chemistry.' (See Benzene.)



benzoic series that the acids of the lactic series bear to the acids of the acetic series. The following are known :—

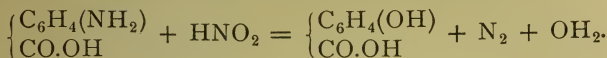


In general behaviour the acids of the salicylic series closely resemble the acids of the lactic series, but are more stable compounds. By the action of acetic chloride they are converted into monaceto-derivatives of the form  $C_nH_{2n-8}(O.C_2H_3O)CO(OH)$ ; etheric acids of the form  $C_nH_{2n-8}(OC_nH_{2n+1})CO(OH)$  may be obtained from them by methods precisely similar to those employed in the preparation of the etheric acids of the lactic series (p. 273).

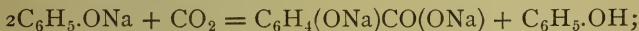
*Salicylic*, *oxybenzoic*, and *paroxybenzoic* acids are produced by oxidation of the isomeric cresols by fusion with potassic hydrate (p. 170); by fusion of the isomeric (ortho-, meta-, and para-) mono-haloid derivatives of benzoic acid with potassic hydrate—thus metabromobenzoic acid yields potassic metoxybenzoate :



and by the action of nitrous acid on heated aqueous solutions of the three isomeric amidobenzoic acids<sup>1</sup> :



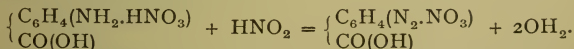
Salicylic acid is also obtained by the action of carbonic anhydride on sodium phenol:



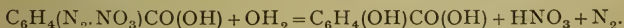
by oxidation of saligenin and salicylic aldehyde; and by saponification of oil of wintergreen (methylic salicylate, p. 151) by potassic hydrate. Paroxybenzoic acid is best prepared by fusing anisic acid with potassic hydrate:



<sup>1</sup> In the case of the monamido-derivatives of the acids of the acetic series, which are similarly converted into the corresponding acids of the lactic series by the action of nitrous acid (p. 270), it is not possible to isolate any intermediate product; but in the case of the monamido-acids derived from the benzoic series and isologous series containing proportionately less hydrogen, the immediate product may usually be isolated. For example, by the action of nitrous acid on a *cold* aqueous or alcoholic solution of amidobenzoic acid to which nitric acid has been added, *diazobenzoic nitrate* is produced:



Similarly a solution of amidobenzoic acid yields *diazobenzoic amido-benzoate*. These diazo-salts are readily decomposed on warming with water: nitrogen is evolved, and the corresponding oxy-acid produced:



The action of nitrous acid appears always to take place in the manner thus indicated: the acid salt of the amido-acid being first converted, by the removal of three units of hydrogen, which are replaced by one unit of nitrogen, into the corresponding diazo-salt, which by the subsequent action of water is converted into the corresponding oxy-acid; in many cases, however, the diazo-salt produced is so unstable apparently that it is at once resolved on formation by the action of water into the oxy-acid. (Compare *Amines, Action of Nitrous Acid on*, p. 333.)

A number of resins (benzoin, acaroid resin, &c.) also furnish this acid when fused with potassic hydrate.

They are crystalline bodies : salicylic acid melts at  $157^{\circ}$  ; oxybenzoic acid at  $199^{\circ}$  ; and paroxybenzoic acid at  $210^{\circ}$ . The aqueous solution of salicylic acid is coloured violet on the addition of ferric chloride, which is not the case with solutions of the isomeric acids. On heating alone, or with water, each of these acids is resolved into phenol and carbonic anhydride : salicylic acid being decomposed at  $220^{\circ}$ – $230^{\circ}$ , paroxybenzoic acid at  $200^{\circ}$ – $210^{\circ}$  ; but oxybenzoic acid<sup>1</sup> only at a much higher temperature. On distillation with  $\text{PCl}_5$  salicylic acid is converted into *chlorobenzoic chloride*,  $\text{C}_6\text{H}_4\text{ClCOCl}$ , which when decomposed by water yields orthochlorobenzoic acid isomeric with metachlorobenzoic acid obtained by chlorinating benzoic acid, and with parachlorobenzoic acid formed by oxidising chlorotoluene.

The isomeric *cresotic* acids are obtained by the simultaneous action of sodium and carbonic anhydride on the isomeric cresols. *Oxymethylbenzoic acid* is prepared by acting on paratoluic acid at  $160^{\circ}$ – $170^{\circ}$  with bromine, and heating the resulting bromotoluic acid,  $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})\text{CO}(\text{OH})$ , with water and alkali. *Mandelic acid* (see p. 234). *Phloretic acid* is produced together with phloroglucin on fusing phloretin with potassic hydrate, phloretin being obtained by heating phloridzin—a glucoside contained in the root-bark of the pear, apple, plum, and cherry tree—with dilute acids:  $\text{C}_{21}\text{H}_{24}\text{O}_{10} + \text{OH}_2 = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_{15}\text{H}_{14}\text{O}_5$ . *Hydrocoumaric acid* is formed by the action of nascent hydrogen on coumaric acid, *hydroparacoumaric* being similarly prepared from paracoumaric acid—an acid obtained from aloes ; the former acid yields salicylic acid on fusion with potassic hydrate, the latter paraoxybenzoic acid. *Phenyllactic acid* is produced by combining cinnamic acid with hypochlorous acid and acting upon the resulting compound  $\text{C}_9\text{H}_9\text{ClO}_3$  with nascent hydrogen. *Thymotic acid* is prepared by the simultaneous action of sodium and carbonic anhydride on thymol (methylpropylphenol).

<sup>1</sup> Oxybenzoic acid distils in great part unchanged when strongly heated, but is in part converted into *anthraflavone*,  $\text{C}_{14}\text{H}_8\text{O}_4 = 2\text{C}_7\text{H}_6\text{O}_3 - 2\text{OH}_2$ , an isomeride of alizarin.

$C_nH_{2n-9}(OH)_2CO(OH)$  OR DIOXYBENZOIC SERIES OF  
MONOBASIC ACIDS.

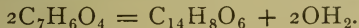
A number of isomeric modifications of the first term of the series—dioxybenzoic acid,  $C_6H_3(OH)_2CO(OH)$ —have been described, but higher terms have not hitherto been investigated. The best known are the following :—

*Protocatechuic acid* (*carbohydroquinonic acid*), produced by fusing kino, catechin, and a number of other resins with potassic hydrate ; also on similar treatment of the monosulphonic acids derived from oxybenzoic and paroxybenzoic acid ; and on oxidation of quinic acid.<sup>1</sup>

*Oxysalicylic acid*, obtained by heating moniodosalicylic acid with potassic hydrate.

*Dioxybenzoic acid*, prepared by fusing the disulphobenzoic acid,  $C_6H_3(SO_3H)_2CO(OH)$ , obtained on heating benzoic acid with concentrated sulphuric acid and phosphoric anhydride at  $230^\circ$ , with potassic hydrate.

These acids are crystalline bodies. On dry distillation protocatechuic acid is resolved into carbonic anhydride and pyrocatechin,  $C_6H_4(OH)_2$  ; oxysalicylic acid, it is stated, yields a mixture of pyrocatechin and hydroquinone ; dioxybenzoic acid yields anthrachrysone (*tetraoxyanthraquinone*):



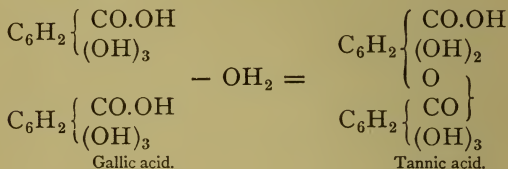
$C_nH_{2n-10}(OH)_3CO(OH)$  OR GALLIC SERIES OF MONO-  
BASIC ACIDS.

GALLIC OR TRIOXYBENZOIC ACID,  $C_6H_2(OH)_3CO(OH)$ , has been produced by the action of potassic hydrate on an aqueous solution of diiodosalicylic acid ; it exists as such in small quantities in many plants, but is most readily obtained from Turkish gall-nuts (*infra*).

Gallic acid crystallises from water in white needles, of the

<sup>1</sup> Quinic acid,  $C_7H_{12}O_6$ , is a crystalline acid contained in cinchona bark, coffee beans, and a number of other vegetable substances.

composition  $C_7H_6O_5.OH_2$ ; its aqueous solution has a slightly acid astringent taste, and is coloured deep blue by ferric salts, but does not precipitate gelatin. Gallic acid is very readily oxidised, and rapidly reduces gold and silver salts to the metallic state. On heating to  $210^\circ$  it is resolved into carbonic anhydride and pyrogallol (*pyrogallic acid*),  $C_6H_3(OH)_3$ . Acetic chloride converts it into *triacetogallic acid*,  $C_6H_2(OC_2H_3O)_3CO(OH)$ . On boiling an aqueous solution of gallic acid to which a small quantity of arsenic acid has been added, *tannic acid* is produced, the arsenic acid remaining unaltered; tannic acid appears to be an etheric anhydride of gallic acid, thus :



By heating with acetic anhydride tannic acid is converted into *pentacetotannic acid*; when boiled with concentrated hydrochloric acid it is reconverted into gallic acid. By heating gallic acid with concentrated sulphuric acid at  $100^\circ$ , so-called *rufigallic acid*,  $C_{14}H_8O_8 = 2C_7H_6O_5 - 2OH_2$ , is produced; rufigallic acid has powerful dyeing properties, yielding with iron and alumina mordants colours similar to those furnished by alizarin, to which indeed it appears to be closely related, as it also yields anthracene when passed over heated zinc dust.

### *Tannic Acids or Tannins.*

This name is applied to a class of substances very widely distributed throughout the vegetable kingdom, which are mostly amorphous, have a slight acid reaction, and are characterised by their astringent taste, by yielding a black-blue or green precipitate or colouration with ferric salts, by precipitating gelatin and albumin from their solutions, and by uniting with animal

membrane to form a mass capable of resisting putrefaction (the membrane is tanned, as it is termed, and converted into leather). At present, however, our knowledge of the composition of these substances is extremely limited. Most of them appear to be glucosides, i.e., they yield a glucose and another substance on boiling with dilute acids. Those which turn ferric salts black-blue usually yield pyrogallol amongst other products on dry distillation, whereas those which turn ferric salts green furnish pyrocatechin.

*Gallotannic Acid or Tannin*, the best known of these compounds, exists in the gall-nuts of *Quercus infectoria* and other species of oak, in the common oak-apple, and in sumach, &c. It is especially abundant in Aleppo galls, from which it may be extracted in the following manner:—A quantity of the finely pulverised gall-nuts is placed in a long narrow glass vessel, provided at the lower end with a plug of cotton-wool, and ordinary ether (containing water and alcohol) poured in. The liquid percolates through the mass and is received in a bottle, in which it separates into two layers. The lower of these is almost colourless, and consists of an aqueous solution of nearly pure tannin; it is separated from the upper, repeatedly washed with ether, and then placed to evaporate over sulphuric acid in vacuo. Tannin thus obtained forms a yellowish, friable, non-crystalline mass, soluble in water, less soluble in alcohol, and very slightly soluble in ether. It exhibits an acid reaction, and has a pure astringent taste; with ferric salts it yields a blue-black precipitate, which is the basis of writing ink. On boiling with dilute acids it yields gallic acid and glucose, being first resolved, it would seem, into glucose and tannic acid, the latter of which is then converted into gallic acid. The same change occurs when powdered galls are mixed with water to a thin paste and exposed to the air in a warm place for two to three months, water being added from time to time to replace that lost by evaporation; and in addition the sugar undergoes alcoholic fermentation. Strecker was led by his analyses to assign the formula  $C_{27}H_{22}O_{17}$  to tannin, and regarded it as a glucoside of gallic acid; but recent experiments show that it more probably has the composition  $C_{34}H_{28}O_{22} = 2C_{14}H_{10}O_9 + C_6H_{12}O_6 - 2OH_2$ , and that it is a glucoside of tannic acid.

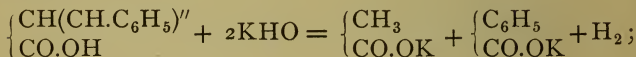


$C_nH_{2n-9}CO(OH)$  OR CINNAMIC SERIES OF MONOBASIC ACIDS.

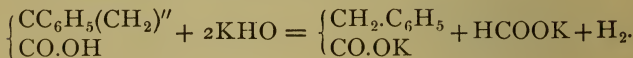
The same relations exist between the acids of this and the benzoic series as between the acids of the acrylic and acetic series.

Three crystalline acids of the composition  $C_8H_7CO(OH)$  are known : *Cinnamic acid*, which exists ready formed in Peru and Tolu balsam, and may also be obtained by oxidation of cinnamon-oil (cinnamic aldehyde), and by the action of sodium and carbonic anhydride on bromocinnamene,  $C_8H_7Br$ ; <sup>1</sup> and *atropic* and *isatropic* acid, which are obtained, together with a basic compound termed *tropine*, on boiling atropine (the alkaloid of *Atropa belladonna*) with baric hydrate solution.

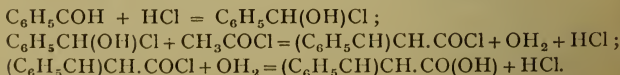
Cinnamic acid melts at  $133^\circ$ ; atropic acid at  $106^\circ$ ; isatropic acid at about  $200^\circ$ . By nascent hydrogen cinnamic acid is converted into hydrocinnamic acid,  $C_9H_{10}O_2$ ; atropic acid into an acid isomeric with the latter. On fusion with potassic hydrate, cinnamic acid yields potassic benzoate and acetate :



whereas atropic acid yields a mixture of potassic formate and the potassic salt of alphetoluic acid :



<sup>1</sup> Cinnamic acid is also produced by a remarkable reaction, by heating benzoic aldehyde with acetic chloride containing hydrochloric acid. The following interpretation of the reaction may be given :



Phenylangelic acid,  $C_{11}H_{12}O_2$ , homologous with cinnamic acid, has been similarly produced by heating benzoic aldehyde with butyric chloride.

$C_nH_{2n-11}CO(OH)$  SERIES OF MONOBASIC ACIDS.

*Phenylpropionic Acid*,  $C_6H_5C_2CO(OH)$ , the sole representative of this series, obtained either by heating  $\alpha$ -bromocinnamic acid with potassic hydrate, or by the union of carbonic anhydride and the sodium derivative of acetenylbenzene (p. 128), is a crystalline acid melting at  $136^\circ$ . Nascent hydrogen converts it into hydrocinnamic acid.

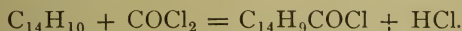
$C_nH_{2n-13}CO(OH)$  OR NAPHTHOIC SERIES OF MONOBASIC ACIDS.

Two isomeric acids of this series,  $\alpha$ - and  $\beta$ -*naphthoic acid*,  $C_{10}H_7CO(OH)$ , are known. These are prepared by distilling the potassic salts of  $\alpha$ - and  $\beta$ -naphthalenesulphonic acid (p. 131) with potassic cyanide, and decomposing the resulting cyanides in the usual manner.  $\alpha$ -Naphthoic acid melts at  $160^\circ$ ;  $\beta$ -naphthoic acid at  $182^\circ$ . In chemical behaviour these acids resemble benzoic acid most closely.

By the simultaneous action of sodium and carbonic anhydride on  $\alpha$ - and  $\beta$ -naphthol (p. 172), two isomeric oxynaphthoic acids,  $C_{10}H_6(OH)CO(OH)$ , are produced.

$C_nH_{2n-19}CO(OH)$  SERIES OF MONOBASIC ACIDS.

A single acid of the series, *anthracenecarboxylic acid*,  $C_{14}H_9CO(OH)$ , has been obtained by heating anthracene with carbonic oxychloride at  $200^\circ$ , and decomposing the resulting acid chloride with water :



It melts at  $206^\circ$ , but is at the same time resolved into anthracene and carbonic anhydride.

$C_nH_{2n}(CO.OH)_2$  OR SUCCINIC SERIES OF DIBASIC ACIDS.

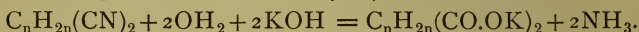
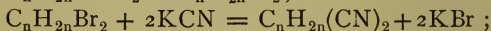
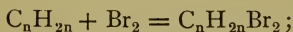
The following terms of this series are known :—

|                             |                                                      |
|-----------------------------|------------------------------------------------------|
| Oxalic acid . . . . .       | (CO.OH) <sub>2</sub>                                 |
| Malonic acid . . . . .      | CH <sub>2</sub> (CO.OH) <sub>2</sub>                 |
| Succinic acid . . . . .     | C <sub>2</sub> H <sub>4</sub> (CO.OH) <sub>2</sub>   |
| Pyrotartaric acid . . . . . | C <sub>3</sub> H <sub>6</sub> (CO.OH) <sub>2</sub>   |
| Adipic acid . . . . .       | C <sub>4</sub> H <sub>8</sub> (CO.OH) <sub>2</sub>   |
| Pimelic acid . . . . .      | C <sub>5</sub> H <sub>10</sub> (CO.OH) <sub>2</sub>  |
| Suberic acid . . . . .      | C <sub>6</sub> H <sub>12</sub> (CO.OH) <sub>2</sub>  |
| Anchoic acid . . . . .      | C <sub>7</sub> H <sub>14</sub> (CO.OH) <sub>2</sub>  |
| Sebacic acid . . . . .      | C <sub>8</sub> H <sub>16</sub> (CO.OH) <sub>2</sub>  |
| Rocellic acid . . . . .     | C <sub>15</sub> H <sub>30</sub> (CO.OH) <sub>2</sub> |

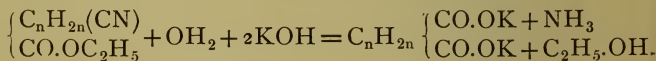
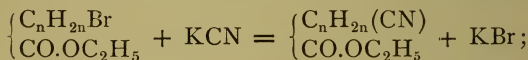
Isomeric modifications of several of these have been obtained.

*Formation.*—1. By oxidation of the primary glycols.<sup>1</sup>

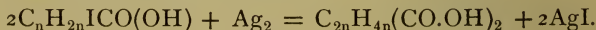
2. From the hydrocarbons of the C<sub>n</sub>H<sub>2n</sub> or olefine series :



3. From the ethylic salts of the mono-haloid derivatives of the acids of the acetic series, in the following manner :



4. By the action of sodium, silver, or copper on the mono-haloid derivatives (preferably the iodo-derivatives) of the acids of the acetic series :



*Properties.*—The acids of the succinic series are crystalline solids. Like all dibasic acids they yield, as previously explained (p. 243), two series of metallic and ethereal salts, acid amides, &c.

<sup>1</sup> Many of the acids of the series—succinic, adipic, pimelic, suberic, and anchoic acid—are obtained by oxidising various fatty and resinous substances—tallow, suet, the oils, &c.—with nitric acid.

They cannot be distilled unchanged, being resolved either into water and the corresponding acid anhydride :



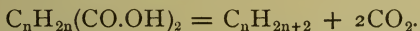
or into carbonic anhydride and an acid of the acetic series :



On electrolysis many of the acids of the series are resolved into an olefine, carbonic anhydride and hydrogen :



When heated with an excess of sodic or baric hydrate they are resolved into a paraffin and carbonic anhydride :



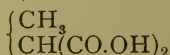
Bromo-substitution-derivatives are obtained by the action of bromine, but the substitution is effected far less readily than in the case of the acids of the acetic series.

OXALIC ACID,  $C_2H_2O_4 = (CO.OH)_2$ .—This acid is present in most plants, sometimes in the free state or as sodic or potassic salt, but more frequently as calcic oxalate. Calcic oxalate is also found in urine and urinary deposits. A large number of complex organic substances, such as sugar, starch, cellulose, &c., yield oxalic acid when oxidised by nitric acid or by fusion with potassic hydrate ; in fact, oxalic acid is now prepared on the large scale by heating sawdust with a mixture of sodic and potassic hydrate. Oxalic acid is produced, as sodic salt, 1. by heating sodium in an atmosphere of dry carbonic anhydride to about the boiling-point of mercury :  $2CO_2 + Na_2 = C_2O_4Na_2$  ; and 2. by heating sodic formate :  $2HCO(ONa) = H_2 + (CO.ONa)_2$ . It is also formed by warming an aqueous solution of cyanogen with hydrochloric acid or an alkali :  $C_2N_2 + 4OH_2 = C_2O_4H_2 + 2NH_3$ , and by oxidation of ethylene glycol.

Oxalic acid crystallises from water in transparent colourless prisms of the composition  $\text{C}_2\text{O}_4\text{H}_2, 2\text{OH}_2$ ; the water of crystallisation is expelled at  $100^\circ$ , and on continued heating the acid is decomposed (see p. 253). Heated in presence of dehydrating agents it is readily resolved into carbonic anhydride, carbonic oxide, and water. Chlorine acting upon an aqueous solution forms hydrochloric acid and carbonic anhydride. Nitric acid scarcely affects oxalic acid, but by most other oxidising agents it is rapidly oxidised to carbonic anhydride and water.

MALONIC ACID,  $\text{C}_3\text{H}_4\text{O}_4 = \text{CH}_2(\text{CO.OH})_2$  (see p. 61).

SUCCINIC ACID,  $\text{C}_2\text{H}_4(\text{CO.OH})_2$ , exists in two isomeric forms, known respectively as



Succinic or ethylenedicarboxylic acid; and Isosuccinic or ethylenedicarboxylic acid.

Succinic acid may be prepared by method 2 (p. 308) from ethylene, and by method 3 from  $\beta$ -chloropropionic acid, isosuccinic acid being prepared from  $\alpha$ -chloropropionic acid (p. 287) by the same method. Succinic acid was originally obtained by dry distillation of amber, in which it exists ready formed; all the acids of the acetic series, from butyric acid upwards, are said to yield succinic and other acids of the series when oxidised by nitric acid. On the large scale it is usually prepared from malic acid by fermentation.

Succinic acid melts at  $180^\circ$ , and when heated to the boiling-point (about  $235^\circ$ ) is resolved into water and succinic anhydride; isosuccinic acid melts at  $130^\circ$ , and when heated to  $150^\circ$  is resolved into carbonic anhydride and propionic acid. Succinic acid is less soluble in water than isosuccinic acid; a solution of sodic succinate yields a red-brown precipitate of ferric succinate with ferric chloride; isosuccinic acid is not precipitated by ferric chloride.

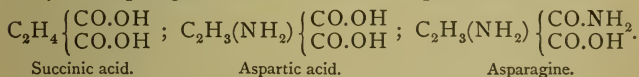
$C_nH_{2n-1}(OH)(CO.OH)_2$  OR MALIC SERIES OF DIBASIC ACIDS.

The acids of this series are trihydric dibasic acids. The following are known :

|                                  |                          |
|----------------------------------|--------------------------|
| Tartronic acid (oxymalonic acid) | $CH(OH)(CO.OH)_2$        |
| Malic acid (oxysuccinic acid)    | $C_2H_3(OH)(CO.OH)_2$    |
| Citramalic acid                  | $C_3H_5(OH)(CO.OH)_2$    |
| Glutanic acid                    |                          |
| Oxyadipic acid                   | $C_4H_7(OH)(CO.OH)_2$    |
| Oxysuberic acid                  | $C_6H_{11}(OH)(CO.OH)_2$ |

MALIC or OXYSUCCINIC ACID,  $C_2H_3(OH)(CO.OH)_2$ .—This acid is most widely distributed throughout the vegetable kingdom, occurring sometimes in the free state, sometimes as potassic, magnesian, or calcic salt ; thus, it is contained in unripe apples, in gooseberries, strawberries, cherries, &c., but is especially abundant in the not quite ripe berries of the mountain ash. It has been obtained by digesting monobromosuccinic acid with argentic oxide and water. Malic acid, like all the acids of the series, is a white crystalline deliquescent substance ; when heated with hydriodic acid, it is reduced to succinic acid.

*Aspartic Acid, Asparagine.*—These two bodies are intimately related to succinic acid, aspartic acid being amidosuccinic acid, and asparagine the acid amide of aspartic acid ; thus:



Asparagine is a crystalline optically active substance, present in asparagus, marsh-mallow, the young shoots of vetches, peas, beans, and many other leguminous plants. When boiled with a mineral acid and water it is resolved into aspartic acid and ammonia. By the action of nitrous acid on an aqueous solution of aspartic acid malic acid is produced.

*Glutamic Acid*,  $C_3H_5(NH_2)(CO.OH)_2$ , is a crystalline acid obtained, together with aspartic acid and other products, on heating gluten, casein, &c., with hydrochloric acid ; nitrous acid converts it into glutanic acid.



$C_nH_{2n-2}(OH)_2(CO.OH)_2$  OR TARTARIC SERIES OF  
DIBASIC ACIDS.

The members of this series are tetrahydric dibasic acids. The following are known :—

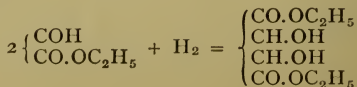
|                                              |                            |
|----------------------------------------------|----------------------------|
| Mesoxalic acid . . . . .                     | (?) $C(OH)_2(CO.OH)_2$     |
| Tartaric acid (dioxysuccinic acid) . . . . . | $C_2H_2(OH)_2(CO.OH)_2$    |
| Homotartaric acid . . . . .                  | } $C_3H_4(OH)_2(CO.OH)_2$  |
| Citratartaric acid . . . . .                 |                            |
| Itatartaric acid . . . . .                   |                            |
| Dioxyadipic acid . . . . .                   | $C_4H_6(OH)_2(CO.OH)_2$    |
| Dioxysuberic acid . . . . .                  | $C_6H_{10}(OH)_2(CO.OH)_2$ |

TARTARIC ACID (*dioxysuccinic acid*),  $C_2H_2(OH)_2(CO.OH)_2$ .—This acid is also very widely distributed throughout the vegetable kingdom, and, together with citric and oxalic acids, usually accompanies malic acid in plants.<sup>1</sup> It is largely employed, and is always prepared from the so-called *crude tartar* or *argol* (hydric potassic tartrate,  $C_4H_5KO_6$ ) which is deposited from fermenting grape juice during the operation of wine making, in the following manner :

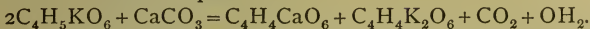
<sup>1</sup> This circumstance alone suggests that a close genetic relation exists between these four acids. Debus has, in fact, recently succeeded in obtaining ethylic tartrate, together with ethylic glycollate, by the action of sodium amalgam on an alcoholic solution of ethylic oxalate. It may be supposed that by the action of the hydrogen generated by the action of the amalgam on the alcohol, ethylic glyoxalate is first produced :



which is in the main converted by the further action of the nascent hydrogen into ethylic glycollate, but also in part converted into ethylic tartrate; thus :



A boiling solution of the acid tartrate is treated with powdered chalk, whereby insoluble calcic tartrate and soluble potassic tartrate are produced :



Calcic chloride solution is then added to the solution of potassic tartrate, and the precipitated calcic tartrate added to the previous precipitate and the whole treated with sufficient sulphuric acid to form calcic sulphate and tartaric acid. Finally, the solution of tartaric acid is separated from the precipitated calcic sulphate and evaporated to crystallisation.

Four modifications of tartaric acid exist, namely :—

1. *Dextrotartaric or ordinary tartaric acid*, so called from its property of causing the plane of polarization of a ray of light to rotate to the right.
2. *Lævotartaric acid*, which rotates the plane of polarization to the left.
3. *Racemic or paratartaric acid*, which is optically inactive, and may be resolved into dextro- and lævo-tartaric acid.
4. *Inactive or mesotartaric acid*, which is also optically inactive, but cannot be resolved into dextro- and lævo-tartaric acid.

The first and third of these occur naturally; the second and fourth are artificially produced.

When dibromosuccinic acid is digested with argentic oxide and water, it is converted into tartaric acid. The acid thus obtained is mesotartaric acid, but Jungfleisch has recently shown that by heating with water at  $175^\circ$  it is converted into racemic acid, which he separated into dextro- and lævo-tartaric acid. He employed succinic acid prepared from ethylene, and has thus proved that it is possible, entirely by artificial means, to produce an optically active substance, which had hitherto been regarded as impossible of accomplishment. Jungfleisch has also shown that by heating with water at  $160^\circ$ , dextrotartaric and racemic acid are both converted into mesotartaric acid.

Dextro- and lævo-tartaric acid have the same specific gravity and solubility in water, and their crystals are bounded by the

same number of faces inclined at exactly the same angles, but certain of the faces which, when the crystals are similarly placed, are to the right in the one modification (in dextro-tartaric acid), are to the left in the other, so that the crystals of these two modifications are to one another as an object and its reflected image. Solutions of the two modifications of equal strength deflect the plane of polarization of a ray of light to an equal extent, but in opposite directions. If a solution containing equal weights of dextro- and lævo-tartaric acid be evaporated to crystallisation, racemic acid is produced,<sup>1</sup> which on the other hand may be resolved into dextro- and lævo-tartaric acid in a variety of ways. Thus, Pasteur has shown that if two solutions containing equal weights of racemic acid are neutralised—the one with ammonia, the other with sodic hydrate, then mixed and evaporated to the crystallising point, crystals of sodic ammonic tartrate are deposited, half of which have certain faces situated on the right, which in the other half are situated on the left; these crystals may be separated by hand, and by dissolving separately the two kinds in water, precipitating by plumbic nitrate, and decomposing the precipitates of plumbic tartrate by dilute sulphuric acid, solutions are obtained which, on evaporation yield respectively dextro-tartaric and lævo-tartaric acid.

The crystals of dextro- and lævo-tartaric acid are anhydrous; those of racemic acid have the composition  $C_4H_6O_6, OH_2$ . Racemic acid is less soluble in water than tartaric acid, and calcic racemate is insoluble in acetic acid, which dissolves calcic tartrate.

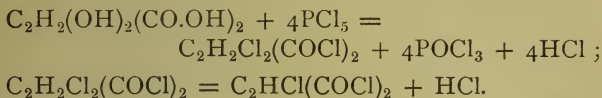
By heating tartaric acid with various alcohols, corresponding ethereal salts,  $C_2H_2(OH)_2(CO.OR')_2$ , &c., are produced.

When tartaric acid is heated with acetic chloride, *diacetotartaric acid*,  $C_2H_2(O.C_2H_3O)_2(CO.OH)_2$ , is formed, but converted at the temperature to which it is necessary to heat in order to complete the reaction into diacetotartaric anhydride,  $C_2H_2(O.C_2H_3O)_2(CO)_2O$ . Ethylic tartrate similarly treated yields either *ethylic acetotartrate* or *ethylic diaceto-*

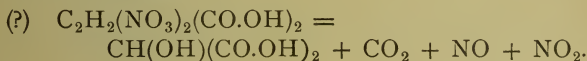
<sup>1</sup> Racemic acid is present together with dextrotartaric acid in certain tartars.

*tartrate*  $C_2H_2(OC_2H_3O)_2(CO.OC_2H_5)_2$ , according to the amount of acetic chloride used.

When distilled with phosphorus pentachloride, tartaric acid is converted into *chloromaleic chloride*:

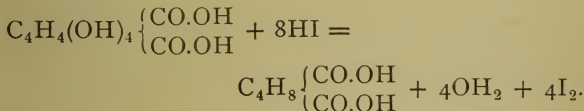


Tartaric acid is carbonised by concentrated sulphuric acid ; it is very readily oxidised by all oxidising agents ; concentrated nitric acid converts it into so-called nitro-tartaric acid,  $C_2H_2(NO_3)_2(CO.OH)_2$ , which spontaneously breaks up into tartronic acid, carbonic anhydride, and oxides of nitrogen :



*Saccharic and Mucic Acid (tetraoxyadipic acid)*,  $C_6H_{10}O_8 = C_4H_4(OH)_4 \begin{Bmatrix} CO.OH \\ CO.OH \end{Bmatrix}$ . The formation of these two isomeric

acids on oxidation of various sugars has previously been noticed (p. 189 et seq.). Saccharic acid, although solid, cannot be obtained in crystals ; it is very soluble, even in cold water. Mucic acid crystallises readily, and is sparingly soluble in cold water. When heated with a concentrated solution of hydriodic acid mucic acid is reduced to adipic acid :



Ethyllic saccharate,  $C_4H_4(OH)_4(CO.OC_2H_5)_2$ , prepared by passing hydrochloric acid into a solution of saccharic acid in alcohol, is converted by acetic chloride into ethyllic tetraceto-saccharate,  $C_4H_4(O.C_2H_3O)_4(CO.OC_2H_5)_2$ .

$C_nH_{2n-2}(CO.OH)_2$  OR FUMARIC SERIES OF DIBASIC ACIDS.

The acids of this series bear the same relation to the acids of the succinic series that the acids of the acrylic series bear to the acids of the acetic series. Thus they unite with nascent hydrogen, forming corresponding acids of the succinic series; they unite with (a) the haloid acids and (b) halogens, forming (a) mono- and (b) di-haloid substitution-derivatives of corresponding acids of the succinic series; and they unite with hypochlorous acid to form monochlorinated acids of the malic series. The following are known :—

|                 |   |   |   |                     |
|-----------------|---|---|---|---------------------|
| Fumaric acid    | . | . | . | } $C_2H_2(CO.OH)_2$ |
| Maleic acid     | . | . | . |                     |
| Citraconic acid | . | . | . | } $C_3H_4(CO.OH)_2$ |
| Itaconic acid   | . | . | . |                     |
| Mesaconic acid  | . | . | . |                     |

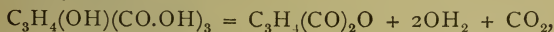
FUMARIC AND MALEIC ACID,  $C_2H_2(CO.OH)_2$ , are produced<sup>1</sup> by the withdrawal of the elements of water from malic acid,  $C_2H_3(OH)(CO.OH)_2$ ; the former is present in the common fumitory (*Fumaria officinalis*), in *Lichen islandicus*, &c.

When malic acid is heated for some time at  $130^\circ$ – $135^\circ$  it is mainly converted into fumaric acid, but when it is rapidly heated chiefly maleic acid is produced, and passes over with the water. Both are crystalline acids. Maleic acid is very soluble in water; fumaric acid is sparingly soluble. Maleic acid melts at about  $130^\circ$ , and at about  $160^\circ$  is converted into maleic anhydride,  $C_4H_2O_3$ ; fumaric acid melts with difficulty, and at about  $200^\circ$  is also converted into maleic anhydride. Both yield succinic acid when treated with nascent hydrogen, but combine with bromine to form isomeric dibromosuccinic acids. On electrolysis they are resolved into acetylene, carbonic anhydride, and hydrogen.

<sup>1</sup> Fumaric acid is also obtained (as baric salt) on boiling trichlorophenomalic acid with baric hydrate solution. Trichlorophenomalic acid is an acid, said to have the composition  $C_6H_7Cl_3O_5$ , prepared by adding potassic chlorate to a mixture of benzene and sulphuric acid.

CITRACONIC, ITACONIC, and MESACONIC ACID,  $C_5H_6O_4 = C_3H_4(CO.OH)_2$ , are produced by the withdrawal of water and carbonic anhydride from citric acid (p. 318) :—

When citric acid is rapidly distilled it is converted into citraconic anhydride :



which readily unites with water, forming citraconic acid. Citraconic acid is converted into itaconic acid by heating with a small quantity of water for some hours, at about  $150^\circ$ , and into mesaconic acid by heating with hydrochloric acid and decomposing the resulting chloropyrotartaric acid by boiling with water. Citraconic and itaconic acid both yield citraconic anhydride on distillation; mesaconic acid may be sublimed unchanged.

Citraconic acid melts at  $80^\circ$ , and is very soluble in cold water.

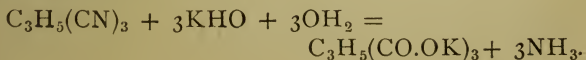
Itaconic acid melts at  $160^\circ$ , and is moderately soluble in cold water.

Mesaconic acid melts at  $200^\circ.5$ , and is only slightly soluble.

With nascent hydrogen they yield the same pyrotartaric acid, but unite with bromine, hypochlorous acid, &c., to form isomeric acids. On electrolysis each of these acids is resolved into allylene,  $C_3H_4$ , carbonic anhydride and hydrogen. The allylene from itaconic and mesaconic acid produces a white crystalline precipitate of the composition  $C_3H_3Ag$  when passed into an ammoniacal solution of argentic nitrate, whereas the allylene from citraconic acid does not affect such a solution.

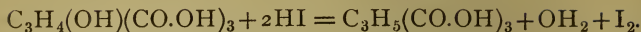
$C_nH_{2n-1}(CO.OH)_3$  OR TRICARBALLYLIC SERIES OF  
TRIBASIC ACIDS.

TRICARBALLYLIC ACID,  $C_6H_8O_6 = C_3H_5(CO.OH)_3$ , the only known acid of the series, is obtained as potassic salt from the tricyanopropane prepared by double decomposition from tribromhydrin (tribromopropane, p. 180) and potassic cyanide ; thus :





Also by heating citric acid with hydriodic acid :



CITRIC ACID (*oxytricarballic acid*),  $\text{C}_3\text{H}_4(\text{OH})(\text{CO.OH})_3$ .—This acid is present in many fruits, together with tartaric, malic, and oxalic acid, but is especially abundant in the lemon, from the juice of which it is always prepared.

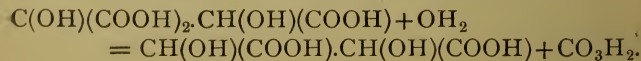
The juice is allowed to ferment a short time, in order to separate mucilaginous matter, &c; it is then filtered and the clear liquid neutralised with calcic carbonate; the insoluble calcic citrate which forms is collected, thoroughly washed, decomposed by the proper quantity of dilute sulphuric acid, and the solution of citric acid evaporated to crystallisation.

Citric acid crystallises from a cold aqueous solution in colourless prisms of the composition  $\text{C}_6\text{H}_8\text{O}_7, \text{OH}_2$ , very soluble in water; it is a tribasic tetrahydric acid. Like malic and tartaric acid it is readily decomposed by sulphuric acid, and on oxidation; when heated it melts, then boils—giving off water, and is converted into *aconitic acid*,  $\text{C}_3\text{H}_3(\text{CO.OH})_3 = \text{C}_3\text{H}_4(\text{OH})(\text{CO.OH})_3 - \text{OH}_2$ , an acid of the  $\text{C}_n\text{H}_{2n-3}(\text{CO.OH})_3$  series. Aconitic acid is found in the roots and leaves of monkshood (*Aconitum Napellus*), and other plants of the same genus; by heating at  $160^\circ - 170^\circ$  it is converted into itaconic acid.

DESOXALIC ACID,  $\text{C}_5\text{H}_6\text{O}_8 = \text{C}(\text{OH})(\text{COOH})_2.\text{CH}(\text{OH})(\text{COOH})$  is obtained as ethylic salt, together with other products, by the action of sodium-amalgam on ethylic oxalate (containing alcohol).

Ethylic desoxalate,  $\text{C}_5\text{H}_3\text{O}_8(\text{C}_2\text{H}_5)_3$ , crystallises in prisms melting at  $85^\circ$ ; it yields a diacetyl derivative on treatment with acetic anhydride.

Desoxalic acid is very unstable: on warming with water it is resolved into racemic and carbonic acids:



Desoxalic acid is crystalline, but very hygroscopic. The baric and calcic salts obtained by decomposing the ethylic salt with baric or calcic hydrate are amorphous.

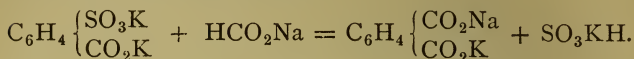
$C_nH_{2n-8}(CO.OH)_2$  OR PHTHALIC SERIES OF DIBASIC ACIDS.

The acids of this series bear the same relation to the acids of the benzoic series and to the hydrocarbons of the benzene series that the acids of the succinic series bear to the acids of the acetic series and to the paraffins. The following are known :—

|                                              |                                     | M.-P.                                 |
|----------------------------------------------|-------------------------------------|---------------------------------------|
| Benzene-dicarboxylic acids.                  | Phthalic or ortho-phthalic acid .   | 185°                                  |
|                                              | Isophthalic or meta-phthalic acid . | above 300°                            |
|                                              | Terephthalic or paraphthalic acid   | sublimes, without melting, above 300° |
| $C_6H_4(CO.OH)_2$                            |                                     |                                       |
| Toluene-dicarboxylic acids.                  | Mesidic or uvitic acid . . .        | 287°-288°                             |
|                                              | Xylylidic acid . . .                | 280°-283°                             |
|                                              | Isoxylylidic acid . . .             | 375°                                  |
| $C_6H_3(CH_3)(CO.OH)_2$                      |                                     |                                       |
| Cumidic acid . . . $C_6H_2(CH_3)_2(CO.OH)_2$ |                                     | sublimes without melting              |

PHTHALIC ACID is produced, together with a small quantity of terephthalic acid, on oxidising a mixture of benzene, or benzoic acid, and formic acid by sulphuric acid and manganic oxide (p. 115); and by oxidation of naphthalene, naphthalene dichloride, alizarin, &c., by nitric acid. It crystallises in plates or prisms, and is sparingly soluble in cold water. On distillation it is converted into phthalic anhydride,  $C_8H_4O_3$ ; it unites with nascent hydrogen, forming *hydrophthalic acid*,  $C_6H_6(CO.OH)_2$ ; when boiled with an oxidising mixture of potassic dichromate and sulphuric acid, it is entirely decomposed.

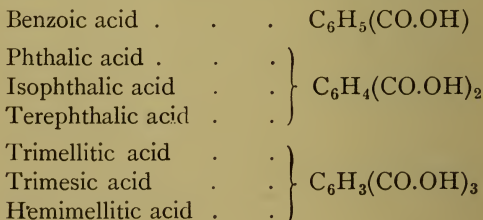
ISOPHTHALIC ACID is obtained by oxidation of meta- (iso-) xylene, and by fusing the potassic salt of metasulphobenzoic acid<sup>1</sup> with sodic formate :



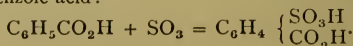
It crystallises in slender white needles, less soluble in water than phthalic acid.

TEREPHTHALIC ACID is produced by oxidation of paraxylene, camphor cymene, and a number of other hydrocarbons of the benzene series, and on fusion of potassic parasulphobenzoate with sodic formate. It is a white amorphous powder, almost insoluble in water. The baric salt of this acid, and of phthalic acid, are very difficultly soluble, even in boiling water ; baric isophthalate, however, is excessively soluble. Isophthalic and terephthalic acid are scarcely affected when heated with an oxidising mixture of potassic dichromate and sulphuric acid.

Phthalic, isophthalic, and terephthalic acids form the second term of a series of acids derived from benzene by the substitution of H by (CO.OH), of which benzoic (benzenecarboxylic) acid is the first, and mellitic (benzenehexacarboxylic) acid the last term. With one exception all the terms of this series are known ; they are as follows :—



<sup>1</sup> This acid is produced, together with a relatively small quantity of the isomeric parasulphobenzoic acid, by the action of sulphuric anhydride on benzoic acid :



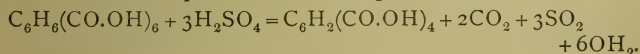
|                   |   |   |   |                   |
|-------------------|---|---|---|-------------------|
| Pyromellitic acid | . | . | } | $C_6H_2(CO.OH)_4$ |
| Prehnitic acid    | . | . |   |                   |
| Mellophanic acid  | . | . |   |                   |
| Unknown acid      | . | . |   | $C_6H(CO.OH)_5$   |
| Mellitic acid     | . | . |   | $C_6(CO.OH)_6$    |

All these acids yield benzene when heated with a slight excess of lime:



MELLITIC ACID (*benzenehexacarboxylic acid*)  $C_{12}H_6O_{12} = C_6(CO.OH)_6$ .—The aluminic salt of this acid constitutes the rare mineral *mellite* or *honey-stone*, found in beds of lignite. Mellitic acid has been obtained, it is said, by oxidising carbon. It crystallises in small white needles, soluble in water and alcohol; it is a hexabasic acid, and furnishes a variety of normal and acid metallic and ethereal salts and amides. On distillation with phosphorus pentachloride it yields the acid chloride,  $C_6(COCl)_6$ .

By the action of nascent hydrogen mellitic acid is converted into *hydromellitic acid*,  $C_6H_6(CO.OH)_6$ , which, when treated with concentrated sulphuric acid, furnishes the two isomeric tetrabasic acids—prehnitic and mellophanic acid:



Pyromellitic acid, the third benzenetetracarboxylic acid, is obtained on heating mellitic acid.

Similarly, prehnitic acid unites with hydrogen, forming *hydro-prehnitic acid*,  $C_6H_8(CO.OH)_4$ , which, on treatment with sulphuric acid, yields tribasic trimesic acid,  $C_6H_3(CO.OH)_3$ , and on heating is resolved into carbonic anhydride and isophthalic acid. The isomeric mellophanic acid furnishes in a similar manner tribasic hemimellitic acid and dibasic phthalic acid. Hydropyromellitic acid,  $C_6H_6(CO.OH)_4$ , is converted into trimellitic and phthalic acid on treatment with sulphuric acid.

When hydropyromellitic acid is distilled it is converted into *tetrahydrophthalic anhydride*, which on boiling with water, yields dibasic tetrahydrophthalic acid,  $C_6H_8(CO.OH)_2$ . This

acid unites with nascent hydrogen, forming hexahydrophthalic acid,  $C_6H_{10}(CO.OH)_2$ , which contains only two units of hydrogen less than suberic acid; thus:

|                            |   |                           |                      |
|----------------------------|---|---------------------------|----------------------|
| Derivatives of<br>Benzene. | { | Suberic acid . . .        | $C_6H_{12}(CO.OH)_2$ |
|                            |   | Hexahydrophthalic acid .  | $C_6H_{10}(CO.OH)_2$ |
|                            |   | Tetrahydrophthalic acid . | $C_6H_8(CO.OH)_2$    |
|                            |   | Hydrophthalic acid . . .  | $C_6H_6(CO.OH)_2$    |
|                            |   | Phthalic acid . . .       | $C_6H_4(CO.OH)_2$    |

When bromine is added to the aqueous solution of tetrahydrophthalic acid bromomalophthalic acid,  $C_6H_8Br(OH)(CO.OH)_2$ , is formed; when this acid is heated with baric hydrate solution, the baric salt of *tartrophthalic acid*,  $C_6H_8(OH)_2(CO.OH)_2$ , is obtained, which is an acid bearing the same relation to hexahydrophthalic acid that tartaric acid bears to succinic acid.

*Summary.*—On comparing the properties of the various isologous primary series of acids, it is at once evident that the relations between them are precisely similar in character to the relations which obtain amongst the various isologous series of hydrocarbons.

Like the hydrocarbons of the paraffin series the acids of the corresponding series, namely, those of the acetic, succinic, and tricarballic series, are saturated compounds, and of considerable stability; the acids of the benzoic and phthalic series evidently correspond to the hydrocarbons of the benzene series; and the analogy between the acids of the acrylic and fumaric series and the hydrocarbons of the acetylene series, and between the acids of the cinnamic series and the hydrocarbons of the cinnamene series, for example, is equally obvious.

The modification which the acids of the various primary series undergo when chlorine, or bromine, is introduced in place of hydrogen is of the same character as that which occurs when the corresponding hydrocarbons are submitted to like treatment.

Similarly, the modification in properties which the acids of the various primary series undergo on conversion into acids

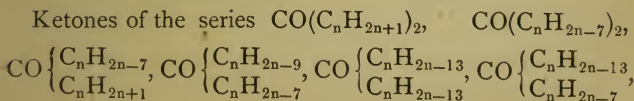
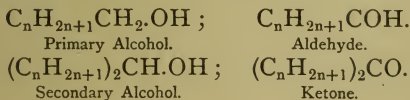
of secondary series, i.e. into acids of the lactic, tartaric, or oxybenzoic series, &c., by the introduction of (OH) in place of H, is in all respects analogous to that which occurs on conversion of the hydrocarbons into alcohols; the secondary acids so formed are less stable than the primary acids from which they are derived, and, as a rule, are far more readily oxidised than the latter.

The relations between the successive terms of each homologous series of acids are apparently of the same character as those which exist between the successive terms of the homologous series of hydrocarbons and alcohols, &c. At present, however, in most cases, only the first few terms of each homologous series are known, and our knowledge of the properties of the higher homologues is unfortunately extremely deficient.

## CHAPTER X.

### KETONES.

THE KETONES bear the same relation to the aldehydes that the secondary monohydric alcohols bear to the primary monohydric alcohols, being derived from the secondary alcohols by oxidation in the same manner that the aldehydes are derived from the primary alcohols; they may be regarded as aldehydes in which H in the COH group has been replaced by a monad hydrocarbon group or radicle:





and a few derived from dibasic acids are known, but our chief knowledge is of the ketones of the  $\text{CO}(\text{C}_n\text{H}_{2n+1})_2$  series, the best known of which are enumerated in the following list :—

|                                  |                                                                                                                                     | B.-P.                                          |
|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| Dimethyl ketone (acetone)        | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \right.$                                                 | $56^\circ$                                     |
| Methyl-ethyl ketone              | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ \text{C}_2\text{H}_5 \end{array} \right.$                                        | $81^\circ$                                     |
| Diethyl ketone (propione)        | $\text{CO} \left\{ \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right.$                               | $100^\circ$                                    |
| Methyl-propyl ketone             | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \right.$                           | $101^\circ$                                    |
| Methyl-isopropyl ketone          | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}(\text{CH}_3)_2 \end{array} \right.$                                    | $93^\circ$                                     |
| Methyl-butyl ketone              | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \right.$                | $127^\circ$                                    |
| Propyl-ethyl ketone              | $\text{CO} \left\{ \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \right.$                  | $128^\circ$                                    |
| Methyl-amyl ketone               | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ (\text{C}_5\text{H}_{11})^\alpha \end{array} \right.$                            | $155^\circ$                                    |
| Dipropyl ketone (butyrone)       | $\text{CO} \left\{ \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \right.$     | $144^\circ$                                    |
| Diisopropyl ketone               | $\text{CO} \left\{ \begin{array}{c} \text{CH}(\text{CH}_3)_2 \\ \text{CH}(\text{CH}_3)_2 \end{array} \right.$ (?)                   | $135^\circ\text{--}137^\circ$                  |
| Diethylated acetone              | $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}(\text{C}_2\text{H}_5)_2 \end{array} \right.$                           | $138^\circ$                                    |
| Diisobutyl ketone (valerone)     | $\text{CO} \left\{ \begin{array}{c} \text{CH}_2\text{CH}(\text{CH}_3)_2 \\ \text{CH}_2\text{CH}(\text{CH}_3)_2 \end{array} \right.$ | $181^\circ$                                    |
| Diamyl ketone (caprone)          | $\text{CO} \left\{ \begin{array}{c} (\text{C}_5\text{H}_{11})^\alpha \\ (\text{C}_5\text{H}_{11})^\alpha \end{array} \right.$       | $220^\circ$                                    |
| Methyl-nonyl ketone <sup>1</sup> | (?) $\text{CO} \left\{ \begin{array}{c} \text{CH}_3 \\ (\text{C}_9\text{H}_{19})^\alpha \end{array} \right.$                        | $224^\circ$                                    |
| Dinonyl ketone                   | (?) $\text{CO} \left\{ \begin{array}{c} (\text{C}_9\text{H}_{19})^\alpha \\ (\text{C}_9\text{H}_{19})^\alpha \end{array} \right.$   | melts at $58^\circ$<br>boils above $350^\circ$ |

<sup>1</sup> This ketone, prepared by distilling a mixture of the calcic salts of acetic and capric acids, is identical with the chief constituent of oil of rue.

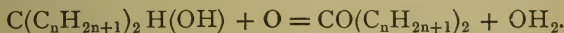
The series  $\text{CO}(\text{C}_n\text{H}_{2n-7})_2$  includes :—

|                                                    |                                                                                                                                       | Melting-point. |
|----------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|----------------|
| Diphenyl ketone<br>(benzophenone) }                | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \right.$                                 | $48^\circ$     |
| { Phenyl-tolyl ketone . . .                        | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_4\cdot\text{CH}_3 \end{array} \right.$                 | $57^\circ$     |
| { Phenyl-benzyl ketone (de-<br>oxybenzoin) . . . } | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CH}_2\cdot\text{C}_6\text{H}_5 \end{array} \right.$                 | $45^\circ$     |
| Dibenzyl ketone . . .                              | $\text{CO} \left\{ \begin{array}{c} \text{CH}_2\cdot\text{C}_6\text{H}_5 \\ \text{CH}_2\cdot\text{C}_6\text{H}_5 \end{array} \right.$ | $30^\circ$     |

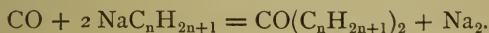
The following terms of the  $\text{CO} \left\{ \begin{array}{c} \text{C}_n\text{H}_{2n-7} \\ \text{C}_n\text{H}_{2n+1} \end{array} \right.$  series are known :—

|                                              |                                                                                                                              | B.-P.       |
|----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|-------------|
| Methyl-phenyl ketone<br>(acetophenone) . . . | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CH}_3 \end{array} \right.$                                 | $199^\circ$ |
| { Ethyl-phenyl ketone . . .                  | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right.$                        | $210^\circ$ |
| { Methyl-benzyl ketone . . .                 | $\text{CO} \left\{ \begin{array}{c} \text{CH}_2\cdot\text{C}_6\text{H}_5 \\ \text{CH}_3 \end{array} \right.$                 | $215^\circ$ |
| { Propyl-phenyl ketone . . .                 | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3 \end{array} \right.$ | $221^\circ$ |
| { Ethyl-benzyl ketone . . .                  | $\text{CO} \left\{ \begin{array}{c} \text{CH}_2\cdot\text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right.$        | $221^\circ$ |
| Isobutyl-phenyl ketone . . .                 | $\text{CO} \left\{ \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{CH}_2\cdot\text{CH}(\text{CH}_3)_2 \end{array} \right.$    | $226^\circ$ |

*Formation.*—1. By oxidation of the secondary monohydric alcohols :

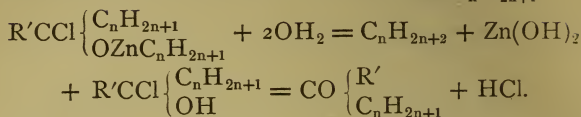
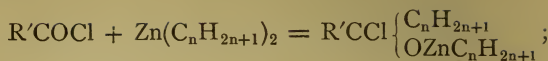


2. By the action of carbonic oxide on the sodium organo-metallic compounds :

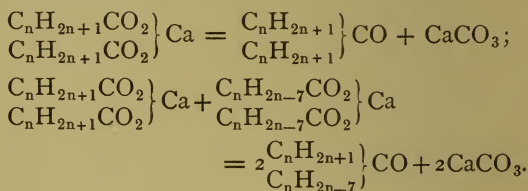


This method has hitherto only been applied to the preparation of ketones of the series  $\text{CO}(\text{C}_n\text{H}_{2n+1})_2$ .

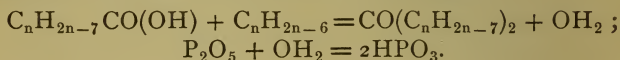
3. By the action of the zinc organo-metallic compounds on the acid chlorides :



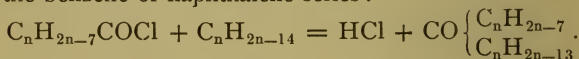
4. By distillation of the baric or calcic salts of the mono-basic monohydric acids, or of mixtures of the salts of two different monobasic acids, thus :



5. By heating a mixture of an acid of the benzoic or naphthoic series and a hydrocarbon of the benzene or naphthalene series with phosphoric anhydride :



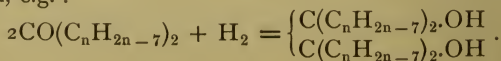
6. By the action of zinc on a mixture of the chloride of an acid of the benzoic or naphthoic series and a hydrocarbon of the benzene or naphthalene series :



*Properties.*—I. By the action of nascent hydrogen (evolved from sodium amalgam and water) the ketones are converted into secondary monohydric alcohols :

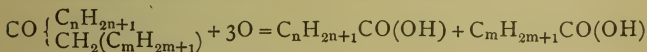


at the same time a dihydric alcohol (or pinacone) is produced, e.g. :



2. The ketones are especially characterised by their behaviour on oxidation—

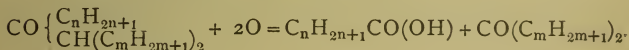
*Law of Oxidation of the Ketones.*—The law may be stated in the following general terms :—On oxidising the ketones one of the hydrocarbon groups in combination with the CO group is converted by the assumption of OH into the corresponding monobasic acid ; the other is split off and separately oxidised. It appears that it is always the less stable (usually the more complex) hydrocarbon group which is thus split off. In the case of the ketones of the  $\text{CO}(\text{C}_n\text{H}_{2n+1})_2$  series, which furnish acids of the acetic series on oxidation, if this group is derived from a primary alcohol it is converted into the acid of the acetic series containing the same number of units of carbon :<sup>1</sup>



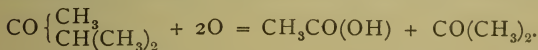
Methyl-propyl ketone, for example, yields acetic and propionic acids:



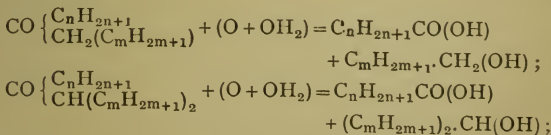
If the hydrocarbon group is derived from a secondary alcohol it is oxidised to the corresponding ketone :



Thus methyl-isopropyl ketone yields acetic acid and acetone:



<sup>1</sup> Probably the oxidation does not take place at a single stage, but the ketone is perhaps in the first place resolved by the combined action of the nascent oxygen and water (or it may be by the action of hydric peroxide) into an acid and an alcohol in the manner indicated by the equations :



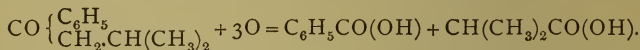
the alcohol thus formed being at once further oxidised.

Finally, if the hydrocarbon group is derived from a tertiary alcohol, we may expect that it will be ultimately oxidised to acids of the acetic series containing fewer units of carbon, as are the tertiary monohydric alcohols (pp. 149, 216).

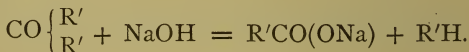
The ketones of other series exhibit a precisely similar behaviour; thus ethyl-phenyl ketone yields benzoic and acetic acids :



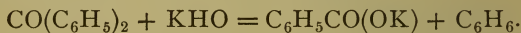
and isobutyl-phenyl ketone yields benzoic and isobutyric acids :



3. When heated with soda-lime, or fused potassic hydrate, the ketones are decomposed in the manner indicated by the equation

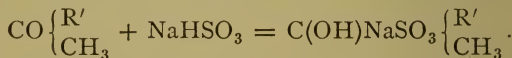


Diphenyl ketone, for example, yields potassic benzoate and benzene on fusion with potassic hydrate :

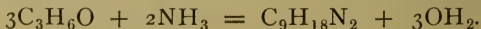


4. The ketones unite with hydrocyanic acid, furnishing cyanides, which on digestion with hydrochloric acid are converted into acids of the lactic series (p. 271).

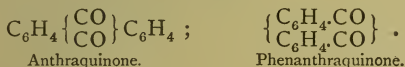
5. The ketones of the form  $\text{CO} \left\{ \begin{array}{c} \text{R}' \\ \text{CH}_3 \end{array} \right.$  (methyl-phenyl ketone excepted) furnish crystalline compounds with hydric ammoniac, potassic, and sodic sulphite, from which the ketone may be liberated by distillation with an alkali :



6. By the action of ammonia on the ketones of the  $\text{CO}(\text{C}_n\text{H}_{2n+1})_2$  series, the oxygen is eliminated in the form of water, and basic compounds are formed ; acetone, for example, is converted into *acetone* :



*Quinones*.—These compounds, of which frequent mention was made in describing the hydrocarbons of the benzene, naphthalene, and anthracene series, are apparently closely related to the ketones, and may, in fact, be regarded as double ketones. Thus anthraquinone and the isomeric phenanthraquinone may be represented in the following manner :



## CHAPTER XI.

## AMINES.

THE AMINES may be regarded as derived from ammonia by the introduction of hydrocarbon groups or radicles in place of hydrogen. Primary, secondary, and tertiary *monamines*, *diamines*, and *triamines* are known ; the nature of the more important series of these compounds will be evident on inspection of the following general formulæ :—

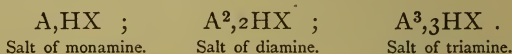
|            | Primary.                                                                                          | Secondary.                                                                                                                                                                                                  | Tertiary.                                                                                                                                                                                                     |
|------------|---------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Monamines. | $\text{N} \left\{ \begin{array}{c} \text{R}' \\ \text{H} \\ \text{H} \end{array} \right.$         | $\text{N} \left\{ \begin{array}{c} \text{R}' \\ \text{R}' \\ \text{H} \end{array} \right.$                                                                                                                  | $\text{N} \left\{ \begin{array}{c} \text{R}' \\ \text{R}' \\ \text{R}' \end{array} \right.$                                                                                                                   |
| Diamines.  | $\text{N}_2 \left\{ \begin{array}{c} \text{R}'' \\ \text{H}_2 \\ \text{H}_2 \end{array} \right.$  | $\text{N}_2 \left\{ \begin{array}{c} \text{R}'' \\ \text{R}'' \\ \text{H}_2 \end{array} \right. ; \quad \text{N}_2 \left\{ \begin{array}{c} \text{R}'' \\ \text{R}'_2 \\ \text{H}_2 \end{array} \right.$    | $\text{N}_2 \left\{ \begin{array}{c} \text{R}'' \\ \text{R}'' \\ \text{R}'' \end{array} \right. ; \quad \text{N}_2 \left\{ \begin{array}{c} \text{R}'' \\ \text{R}'_2 \\ \text{R}'_2 \end{array} \right.$     |
| Triamines  | $\text{N}_3 \left\{ \begin{array}{c} \text{R}''' \\ \text{H}_3 \\ \text{H}_3 \end{array} \right.$ | $\text{N}_3 \left\{ \begin{array}{c} \text{R}''' \\ \text{R}''' \\ \text{H}_3 \end{array} \right. ; \quad \text{N}_3 \left\{ \begin{array}{c} \text{R}''' \\ \text{R}'_3 \\ \text{H}_3 \end{array} \right.$ | $\text{N}_3 \left\{ \begin{array}{c} \text{R}''' \\ \text{R}''' \\ \text{R}''' \end{array} \right. ; \quad \text{N}_3 \left\{ \begin{array}{c} \text{R}''' \\ \text{R}'_3 \\ \text{R}'_3 \end{array} \right.$ |

The amines which have hitherto received the most atten-



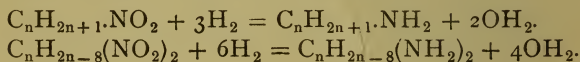
tion are those in which the groups R in these formulæ are the so-called radicles derived from the hydrocarbons of the  $C_nH_{2n+2}$  and  $C_nH_{2n-6}$  series. A large number of the natural alkaloids are tertiary amines.

With few exceptions the amines are basic compounds, uniting with acids to form salts analogous to the ammoniac salts: representing by the symbols A,  $A^2$ ,  $A^3$ , respectively, the amines, diamines, and triamines, and by HX a monobasic acid, such as nitric acid, the proportions in which the amines in the majority of the cases unite with acids to form normal salts is given by the symbols

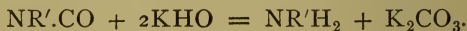


These salts are decomposed by alkalies with separation of the amine, just as the ammoniac salts are decomposed and ammonia separated.

*Formation.*—1. By the reduction of the nitro-substitution-derivatives of the hydrocarbons by ammoniac sulphide, or tin and hydrochloric acid, &c. (p. 48):

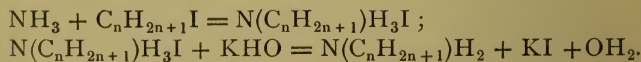


2. By distilling the isocyanates (p. 336) and isocyanurates with potassic hydrate:



These methods are only available for the preparation of primary amines.

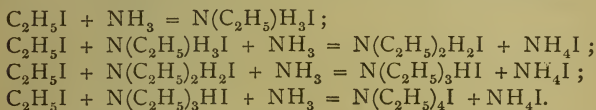
3. By the action of the haloid derivatives of the hydrocarbons on ammonia, the salt produced being subsequently decomposed by potassic hydrate, thus:



This method is available for the preparation of primary, secondary, and tertiary amines (see *Ethylamines*, p. 331).

4. Amines are also produced by the action of ammonia on the aldehydes and ketones, and by various special methods.

*Ethylamine*,  $\text{N}(\text{C}_2\text{H}_5)\text{H}_2$ , *Diethylamine*,  $\text{N}(\text{C}_2\text{H}_5)_2\text{H}$ , and *Triethylamine*,  $\text{N}(\text{C}_2\text{H}_5)_3$ .—When ethylic iodide is heated with an alcoholic solution of ammonia a complex product is obtained, which is the result of the following succession of changes :



When the mixture of iodides thus produced<sup>1</sup> is distilled with potassic hydrate a distillate containing ethylamine, diethylamine, and triethylamine is obtained, which cannot be separated by fractional distillation. If, however, ethylic oxalate is added to the mixture and the whole heated for several days in a closed vessel at  $100^\circ$ , the ethylamine is converted into *diethyloxamide*,  $\text{C}_2\text{O}_2(\text{NH}.\text{C}_2\text{H}_5)_2$ , and the diethylamine into *ethylic diethyloxamate*,  $\text{C}_2\text{O}_2\left\{\begin{smallmatrix} \text{N}(\text{C}_2\text{H}_5)_2 \\ \text{OC}_2\text{H}_5 \end{smallmatrix}\right.$ , whilst the triethylamine remains unaffected. The triethylamine having been distilled off, the residue is cooled in a freezing mixture, and then pressed between linen cloth ; by this means crystalline diethyloxamide is left behind and liquid ethylic diethyloxamate passes through ; the former is purified by recrystallisation from water, the latter by fractional distillation. From the pure diethyloxamide and ethylic diethyloxamate ethylamine and diethylamine are respectively obtained by distillation with potassic hydrate.

Ethylamine is also produced by reducing nitroethane (p. 90), and by distilling ethylic isocyanate with potassic hydrate.

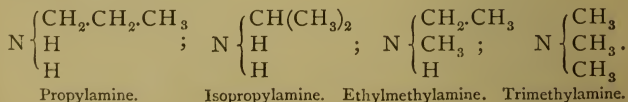
<sup>1</sup> The proportions in which the several products are obtained varies with the amounts of ethylic iodide and ammonia employed and the temperature to which the mixture is heated ; but even when the proportion of ammonia taken is largely in excess of that indicated by the first equation, the product, although mainly ethylammonic iodide, always contains more or less of the other compounds. Ethylic chloride and bromide give rise to a similar series of products.

Ethylamine, diethylamine, and triethylamine are colourless mobile inflammable liquids, which boil respectively at  $19^{\circ}$ ,  $58^{\circ}$ , and  $91^{\circ}$ ; they possess an ammoniacal odour. The two former are very soluble, the latter is sparingly soluble, in water; the solutions are powerfully alkaline, and exhibit most of the properties of an ammonia solution: precipitating various metals from solutions of their salts as hydrates, for example. The chlorides produced by the union of these bases with hydrochloric acid form crystalline double salts with platinic chloride, such as  $2N(C_2H_5)_3Cl, PtCl_4$ ,  $2N(C_2H_5)_2H_2Cl, PtCl_4$ .

*Tetrethylammonic Hydrate*,  $N(C_2H_5)_4.OH$ . — Triethylamine and ethylic iodide combine readily to form tetrethylammonic iodide; from this compound potassic hydrate does not separate triethylamine, but partially converts it by double decomposition into tetrethylammonic hydrate. This latter compound is readily produced in a pure state by digesting the iodide with silver oxide and water, and is obtained in the solid state on evaporating the solution over sulphuric acid in vacuo. The aqueous solution exhibits the closest resemblance to a solution of potassic or sodic hydrate: it is powerfully caustic; precipitates various metallic salts, and is capable of saponifying ethereal salts, &c. Tetrethylammonic hydrate is resolved on heating into triethylamine, ethylene, and water (p. 95):



*Homologues of Ethylamine, &c.*—By the action of the homologues of ethylic iodide (bromide and chloride) on ammonia a series of homologues of the above described amines have been obtained, which, in all respects, bear the closest resemblance to them. Various cases of isomerism present themselves in the series: for example, the two primary monamines, propylamine, and isopropylamine, are isomeric, but are metameric with the secondary monamine ethylmethylaniline and the tertiary monamine trimethylamine:—



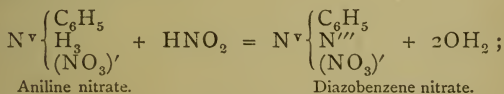
*Phenylamine, Amidobenzene, or Aniline*,  $N(C_6H_5)_2$ .—This

amine was originally obtained by distillation of indigo with potassic hydrate; the botanical name of the indigo plant being *Indigofera anil*, it therefore was termed aniline. It has of late years attained to great importance on account of the numerous and magnificent dyes derived from it, and is prepared on the large scale by the reduction of nitrobenzene by iron and acetic acid. Aniline is a colourless oily liquid of peculiar odour at ordinary temperatures, but at  $-8^{\circ}$  solidifies to a crystalline mass; it boils at  $182^{\circ}$ ; it is only slightly soluble in water. By the action of ethylic iodide it may be converted successively into ethylphenyl-, diethylphenyl-, and triethylphenyl-ammonic iodide. From the two former ethyl- and diethyl-phenyl-amine may be separated by potassic hydrate; the latter is converted into triethylphenylammonic hydrate on treatment with argentic oxide and water. Aniline forms with the various acids well-crystallised salts; similarly, mono- and di-bromaniline are basic compounds and form salts, but the salts of dibromaniline are far less stable than the corresponding salts of bromaniline. The introduction of a third unit of bromine in place of hydrogen reduces the amine to a neutral body: tribromaniline,  $N(C_6H_2Br_3)H_2$ , being incapable of forming salts.

*Action of Nitrous Acid on the Primary Monamines.*—The monamines of the series  $N(C_nH_{2n+1})H_2$  are converted into corresponding monohydric alcohols by the action of nitrous acid:



The monamines derived from the hydrocarbons of the  $C_nH_{2n-6}$  series and isologous series containing proportionately less hydrogen may also be ultimately converted into corresponding alcohols, aniline, for example, yielding phenol; but in the majority of cases an intermediate product—a so-called *diazo-derivative*—may be isolated; if a salt of the monamine be acted upon, a diazo-salt is produced, e.g.:



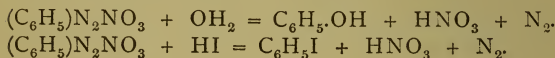
or generally:



If the amine alone be acted upon a so-called *diazo-amido-derivative* results<sup>1</sup>; aniline, for example, is converted into diazo-amidobenzene :



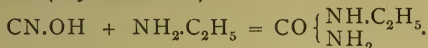
The diazo-derivatives as a class, whether derived from the amines or the amido-acids, are highly unstable bodies: thus they are readily decomposed when heated with anhydrous alcohol, or with water, or with a concentrated aqueous solution of hydriodic acid. The changes which occur in these cases result in the formation of compounds derived from the amido-compounds, the diazo-derivatives of which are acted upon, by the simple replacement of the  $\text{NH}_2$  group by a single unit of hydrogen, by  $\text{OH}$ , or by a unit of iodine; for example :



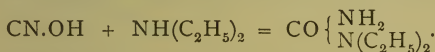
*Formation of Compound Ureas from the Amines.*—Ammonic cyanate,  $\text{CNO}(\text{NH}_4)$ , (formed by the union of ammonia and cyanic acid), it will be remembered, is an exceedingly unstable body, being rapidly converted into the metameric compound urea or carbamide,  $\text{CO}(\text{NH}_2)_2$ , on warming (p. 278). Cyanic acid also combines with the primary and secondary monamines (and diamines); the combination is accompanied by the evolution of much heat, and a series of crystalline bodies—known as *compound ureas*—is produced, bearing the same relation to urea that

<sup>1</sup> Nitrous acid appears to act upon all compounds which may be supposed to contain the  $\text{NH}_2$  group in a similar manner: either the amido-group is immediately converted into the  $(\text{OH})$  group, which is the case when, for example, the acid amides, and the amido-derivatives of the acids of the acetic series are acted upon; or a diazo-derivative is produced, in which case three units of hydrogen are removed and replaced by a single unit of (triad?) nitrogen. Hitherto little attention has been paid to the behaviour of the diamines and triamines with nitrous acid.

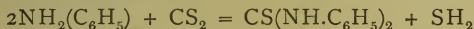
the amines bear to ammonia; thus ethylamine and cyanic acid yield *ethylurea* (*ethylcarbamide*):



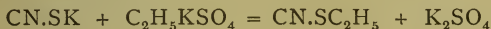
In like manner diethylamine and cyanic acid form *diethylurea*:



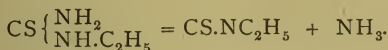
The primary and secondary monamines react with carbonic disulphide forming *compound sulphoureas*; thus, when a mixture of phenylamine and carbonic disulphide is heated, *diphenylsulphocarbamide* is produced:



*Sulphocyanates and Cyanates*.—When a dry mixture of potassic sulphocyanate and potassic ethylic sulphate (potassic sulphovinate) is distilled, *ethylic sulphocyanate* is produced:



An isomeric compound, *ethylic isosulphocyanate*, is obtained by distilling ethyl- or diethyl-sulphocarbamide with phosphoric anhydride:



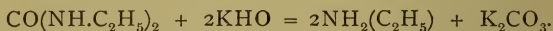
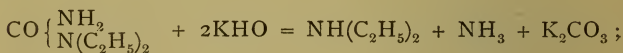
These two reactions may be generalised, but whereas the former is only available for the production of sulphocyanates of the series  $\text{CN.SC}_n\text{H}_{2n+1}$ , the latter appears to be generally available. Isosulphocyanates (*sulphocarbimides*) are also produced by the union of the isocyanides (*carbamines*, p. 93) with sulphur.

The sulphocyanates, which may be represented by the formula  $\text{S} \left\{ \begin{array}{l} \text{R}' \\ (\text{CN}) \end{array} \right.$ , appear always to boil at higher temperatures than the corresponding isosulphocyanates, which are represented by the formula  $\text{N} \left\{ \begin{array}{l} \text{R}' \\ (\text{CS}) \end{array} \right.$ ; thus ethylic sulphocyanate boils at  $146^\circ$ , ethylic isosulphocyanate at  $133^\circ$ . The sulphocyanates are unpleasant smelling liquids; the isosulphocyanates possess most



pungent irritating odours. The sulphocyanates are comparatively inert bodies, and are with difficulty, if at all, attacked by ammonia, for example; the isosulphocyanates, however, combine with the greatest readiness with ammonia and the amines to form compound sulphoureas. Allylic sulphocyanate from mustard-oil (p. 163) is an isosulphocyanate, hence Hofmann applies the generic name of *mustard-oils* to the isosulphocyanates.

By distilling the compound ureas of the form  $\text{CO} \left\{ \begin{smallmatrix} \text{NHR}' \\ \text{NH}_2 \end{smallmatrix} \right.$  and  $\text{CO} \left\{ \begin{smallmatrix} \text{NHR}' \\ \text{NHR}' \end{smallmatrix} \right.$  with phosphoric anhydride a series of isocyanates (*carbimides*) corresponding to the above described isosulphocyanates are obtained; the isocyanates of the series  $\text{CO}.\text{NC}_n\text{H}_{2n+1}$  are also produced by distilling a mixture of potassic cyanate and the potassic ethereal sulphates (*Sulphovinates*) of the form  $\text{C}_n\text{H}_{2n+1}\text{KSO}_4$ . The cyanates corresponding to the sulphocyanates are at present unknown. The isocyanates combine with the amines, forming compound ureas: thus ethylic isocyanate and ethylamine unite, forming a diethylcarbamide isomeric with the diethylcarbamide produced from cyanic acid and diethylamine—the latter compound yields diethylamine, ammonia, and potassic carbonate when boiled with potassic hydrate solution; the former ethylamine and potassic carbonate:



Like cyanic acid the isocyanates are readily polymerised and converted into isocyanurates  $(\text{CO})_3(\text{NR}')_3$ .

### Phosphines.

The phosphines are a series of compounds bearing to phosphine (phosphuretted hydrogen) the same relation that the monamines bear to ammonia. The following primary, secondary, and tertiary methyl- and ethyl- phosphines have

been obtained by the action of methylic and ethylic iodide on phosphine<sup>1</sup> :—

|                      |                |   | B. P.       |
|----------------------|----------------|---|-------------|
| Methylphosphine .    | $P(CH_3)H_2$   | . | $-14^\circ$ |
| Dimethylphosphine .  | $P(CH_3)_2H$   | . | $25^\circ$  |
| Trimethylphosphine . | $P(CH_3)_3$    | . | $41^\circ$  |
| Ethylphosphine .     | $P(C_2H_5)H_2$ | . | $25^\circ$  |
| Diethylphosphine .   | $P(C_2H_5)_2H$ | . | $85^\circ$  |
| Triethylphosphine    | $P(C_2H_5)_3$  | . | $127^\circ$ |

The tertiary phosphines are also produced by the action of the zinc organo-metallic compounds on  $PCl_3$ . The phosphines exhibit the most striking resemblance to the monamines, but are distinguished by their energetic affinities for the negative elements, oxygen, chlorine, &c. Many of them are spontaneously inflammable in air or oxygen. The tertiary phosphines combine with the moniodoparaffins, forming iodides,  $P(C_nH_{2n+1})_4I$ , which are converted into corresponding hydrates,  $P(C_nH_{2n+1})_4.OH$ , on treatment with argentic oxide and water ; these hydrates are powerfully caustic bases.

The following series of products is obtained on oxidation of the above-mentioned ethylphosphines :—

|                            |   |                    |
|----------------------------|---|--------------------|
| Ethylphosphinic acid .     | . | $PO(C_2H_5)(OH)_2$ |
| Diethylphosphinic acid .   | . | $PO(C_2H_5)_2(OH)$ |
| Triethylphosphinic oxide . | . | $PO(C_2H_5)_3$     |

## CHAPTER XII.

### ORGANO-METALLIC COMPOUNDS.

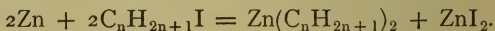
THIS term is applied to an important class of bodies, which may conveniently be regarded as compounds of the metals with

<sup>1</sup> A description of the preparation and properties of these compounds will be found in the *Journal of the Chemical Society* for 1871 and 1872.

hydrocarbon groups or radicles. The metallic compounds of the hypothetical radicles methyl  $(\text{CH}_3)'$  and ethyl  $(\text{C}_2\text{H}_5)'$  have chiefly been studied. The following list of some of the principal organo-metallic compounds will serve to illustrate the nature of these bodies :—

|                                     |                                                           |
|-------------------------------------|-----------------------------------------------------------|
| Sodic ethide <sup>1</sup> . . .     | $\text{NaC}_2\text{H}_5$                                  |
| Magnesian ethide . . .              | $\text{Mg}(\text{C}_2\text{H}_5)_2$                       |
| Zincic ethide . . .                 | $\text{Zn}(\text{C}_2\text{H}_5)_2$                       |
| Mercuric ethide . . .               | $\text{Hg}(\text{C}_2\text{H}_5)_2$                       |
| Mercuric phenide . . .              | $\text{Hg}(\text{C}_6\text{H}_5)_2$                       |
| Mercuric naphthide . . .            | $\text{Hg}(\text{C}_{10}\text{H}_7)_2$                    |
| Stannous ethide . . .               | $\text{Sn}(\text{C}_2\text{H}_5)_2$                       |
| Distannic hexethide . . .           | $\text{Sn}_2(\text{C}_2\text{H}_5)_6$                     |
| Stannic ethide . . .                | $\text{Sn}(\text{C}_2\text{H}_5)_4$                       |
| Stannic phenyltriethide . . .       | $\text{Sn}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_3$ |
| Plumbic ethide . . .                | $\text{Pb}(\text{C}_2\text{H}_5)_4$                       |
| Aluminic methide . . .              | $\text{Al}_2(\text{CH}_3)_6$                              |
| Trimethylarsine . . .               | $\text{As}(\text{CH}_3)_3$                                |
| Diarsentetramethide (cacodyl) . . . | $\text{As}_2(\text{CH}_3)_4$                              |
| Trimethylstibine . . .              | $\text{Sb}(\text{CH}_3)_3$                                |
| Triethylbismuthine . . .            | $\text{Bi}(\text{C}_2\text{H}_5)_3$                       |

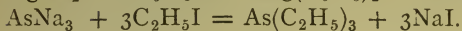
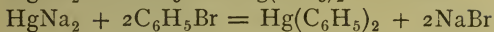
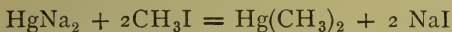
*Formation.*—1. By the action of the metals on the moniodoparaffins. This method is chiefly employed in the preparation of the zinc compounds :



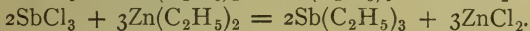
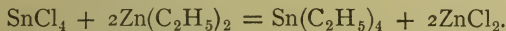
2. By the action of the metals alloyed with potassium or sodium, on the moniodo-derivatives<sup>2</sup> of the hydrocarbons. This method is very generally available, and has been employed in the preparation of the mercury, tin, lead, arsenic, antimony, and bismuth compounds, e.g. :

<sup>1</sup> This compound has not been isolated, and is only known in combination with zincic ethide (see p. 340).

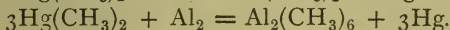
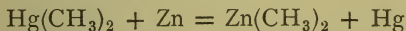
<sup>2</sup> In a few cases the monobromo-derivatives are available.



3. By the action of the zinc organo-metallic compounds on the haloid compounds of the metals. This method is applicable in a very large number of cases ; but has failed when applied to the haloid compounds of copper, iron, silver, and platinum :



4. By the displacement of a metal in an organo-metallic compound by another and more positive metal :

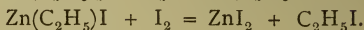
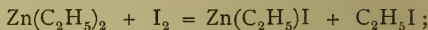


*Zinc Organo-metallic Compounds.*—Of these bodies, which are by far the most important of the organo-metallic compounds, frequent mention has been made in the foregoing pages. The zinc compounds of methyl ( $\text{CH}_3$ ), ethyl ( $\text{C}_2\text{H}_5$ ), propyl ( $\text{C}_3\text{H}_7$ ), isobutyl ( $\text{C}_4\text{H}_9$ )<sup>β</sup>, and isoamyl ( $\text{C}_5\text{H}_{11}$ )<sup>β</sup>, have been obtained.

*Zincic ethide* (zinc ethyl),  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , was originally prepared by Frankland by heating ethylic iodide with granulated zinc in closed vessels at  $100^\circ$ ; a crystalline zincic ethiodide,  $\text{ZnIC}_2\text{H}_5$ , is formed, which decomposes on distillation at about  $150^\circ$  into zincic ethide and iodide. Gladstone and Tribe have recently shown that when zinc foil coated with finely divided copper<sup>1</sup> is employed, the reaction takes place very rapidly and at a much lower temperature. Zincic ethide is a mobile, colourless, spontaneously inflammable liquid, which boils at  $118^\circ$ . It is instantly decomposed by water with formation of ethane and zincic hydrate. When carefully treated with dry oxygen it is first converted into zincic ethylethylate,  $\text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix} \right.$ , and finally

<sup>1</sup> By immersion in a dilute aqueous solution of cupric sulphate.

into zincic ethylate,  $\text{Zn} \left\{ \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix} \right.$ . Iodine acts upon it in the following manner:—



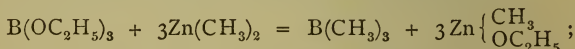
The employment of the zincorgano-metallic compounds as synthetic agents has hitherto been successful in three distinct directions:—

1. To effect the replacement of the halogens in various haloid compounds by  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , &c. ; of which many instances have been given in previous pages.

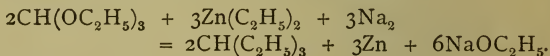
2. To effect the replacement of oxygen by  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , &c., as in the formation of the acids of the lactic series from oxalic acid (p. 271).

3. To effect the replacement of  $\text{OCH}_3$ ,  $\text{OC}_2\text{H}_5$ ,  $\text{OC}_n\text{H}_{2n+1}$  by  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_n\text{H}_{2n+1}$ ; as examples of which may be quoted :

1. the conversion of boric ethylate into boric methide :



2. the formation of the paraffin trimethylmethane from ethylic orthoformate (p. 255), zincic ethide and sodium :



*Sodic Ethide.*—When sodium is enclosed in a tube (previously filled with coal gas) with about ten times its weight of zincic ethide, in the course of a few days it is dissolved and zinc deposited : the product is a solution of a compound of sodic ethide and zincic ethide— $\text{NaC}_2\text{H}_5$ ,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ —in an excess of the latter. This compound is deposited in crystals when the liquid is exposed to a temperature of  $0^\circ$ . All the attempts to separate sodic ethide from this compound have been unsuccessful. Sodium has a similar action on the homologues<sup>1</sup> of zincic ethide, and analogous compounds are formed by the action of the metals potassium and lithium.

<sup>1</sup> The homologues of zincic ethide are best obtained in a pure state by the action of zinc on the corresponding mercury compounds. They are in all respects analogous compounds.

*Mercury Organo-metallic Compounds.*—When methylic iodide is exposed to sunlight in contact with mercury, the two substances combine to form *mercuric iodomethide*,  $\text{HgICH}_3$ . Strange to say, this combination cannot be effected by the aid of heat. Similarly, *mercuric iodoethide* may be obtained by exposing ethylic iodide and mercury to diffused daylight only; in bright sunlight the products are mercuric iodide and diethyl (tetraene, p. 81).

*Mercuric Methide*,  $\text{Hg}(\text{CH}_3)_2$ , *Mercuric Ethide*,  $\text{Hg}(\text{C}_2\text{H}_5)_2$ .—These bodies are obtained by the action of methylic and ethylic iodide on sodium amalgam. The iodides have no perceptible action on the amalgam at ordinary temperatures, but on the addition of a few drops of acetic ether, a brisk action, accompanied by the evolution of heat, sets in, and the iodide is rapidly converted into the organo-mercury compound. The function of the acetic ether in the reaction is not understood; it is found in undiminished quantity at the close of the reaction.

Mercuric methide and ethide are highly stable bodies; they are colourless liquids, insoluble in water, but soluble in alcohol: the former boils at  $93^\circ$ – $96^\circ$ , the latter at  $158^\circ$ – $160^\circ$ . In contact with mercuric iodide, mercuric methide is converted into mercuric iodomethide.

### Organo-silicon Compounds.

The great similarity in chemical functions between silicon and carbon has during the last few years been strikingly illustrated by the discovery of a number of organo-silicon compounds<sup>1</sup> related not only in composition but also in properties to various well-known carbon compounds. It will be evident on inspection of the following lists how close is the analogy between the two series:—

---

<sup>1</sup> Descriptions of the preparation and properties of these compounds will be found in Watts's *Dictionary of Chemistry*, and in the *Journal of the Chemical Society* for 1871, 1872, and 1873.



| SILICON COMPOUNDS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | CORRESPONDING CARBON COMPOUNDS                                                                                                                                                                                                                                                                                                                              |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{SiH}_4$ .<br>$\text{SiHCl}_3$ .<br>$\text{SiCl}_4$ .<br>$\text{SiI}_4$ .<br>$\text{SiI}_6$ .<br>$\text{Si}(\text{OC}_2\text{H}_5)_4$ .<br>$\text{Si}(\text{CH}_3)_4$ .<br>$\text{Si}(\text{C}_2\text{H}_5)_4$ .<br>$\text{Si}_2(\text{C}_2\text{H}_5)_6$ .<br>$\text{Si} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_4\text{Cl} \\ (\text{C}_2\text{H}_5)_3 \end{smallmatrix} \right.$ .<br>$\text{Si} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_4(\text{C}_2\text{H}_3\text{O}_2) \\ (\text{C}_2\text{H}_5)_3 \end{smallmatrix} \right.$ .<br>$\text{Si} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_4\text{OH} \\ (\text{C}_2\text{H}_5)_3 \end{smallmatrix} \right.$ .<br>$\text{SiH}(\text{OC}_2\text{H}_5)_3$ .<br>$\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_3$ .<br>$\text{Si}(\text{C}_2\text{H}_5)(\text{OC}_2\text{H}_5)_3$ .<br>$\text{HSiO}(\text{OH})$ .<br>$\text{CH}_3\text{SiO}(\text{OH})$ .<br>$\text{C}_2\text{H}_5\text{SiO}(\text{OH})$ .<br>$\text{Si}_2\text{H}_2\text{O}_4$ . | Methane<br>Chloroform<br>Carbonic chloride<br>Hexachlorethane<br>Ethylic orthocarbonate<br>Tetramethylmethane (pentane)<br><i>(Unknown)</i><br><i>(Unknown)</i><br>Monochlorononane<br>Nonylic acetate<br>Nonylic alcohol<br>Ethylic orthoformate<br>Ethylic orthacetate<br><i>(Unknown)</i><br>Formic acid<br>Acetic acid<br>Propionic acid<br>Oxalic acid |
| $\text{CH}_4$ .<br>$\text{CHCl}_3$ .<br>$\text{CCl}_4$ .<br>$\text{C}_2\text{Cl}_6$ .<br>$\text{C}(\text{OC}_2\text{H}_5)_4$ .<br>$\text{C}(\text{CH}_3)_4$ .<br>$\text{C}(\text{C}_2\text{H}_5)_4$ .<br>$\text{C}_2(\text{C}_2\text{H}_5)_6$ .<br>$\text{C}_9\text{H}_{19}\text{Cl}$ .<br>$\text{C}_9\text{H}_{19}(\text{C}_2\text{H}_3\text{O}_2)$ .<br>$\text{C}_9\text{H}_{19}\text{OH}$ .<br>$\text{CH}(\text{OC}_2\text{H}_5)_3$ .<br>$\text{C}(\text{CH}_3)(\text{OC}_2\text{H}_5)_3$ .<br>$\text{C}(\text{C}_2\text{H}_5)(\text{OC}_2\text{H}_5)_3$ .<br>$\text{HCO}(\text{OH})$ .<br>$\text{CH}_3\text{CO}(\text{OH})$ .<br>$\text{C}_2\text{H}_5\text{CO}(\text{OH})$ .<br>$\text{C}_2\text{H}_2\text{O}_4$ .                                                                                                                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                             |

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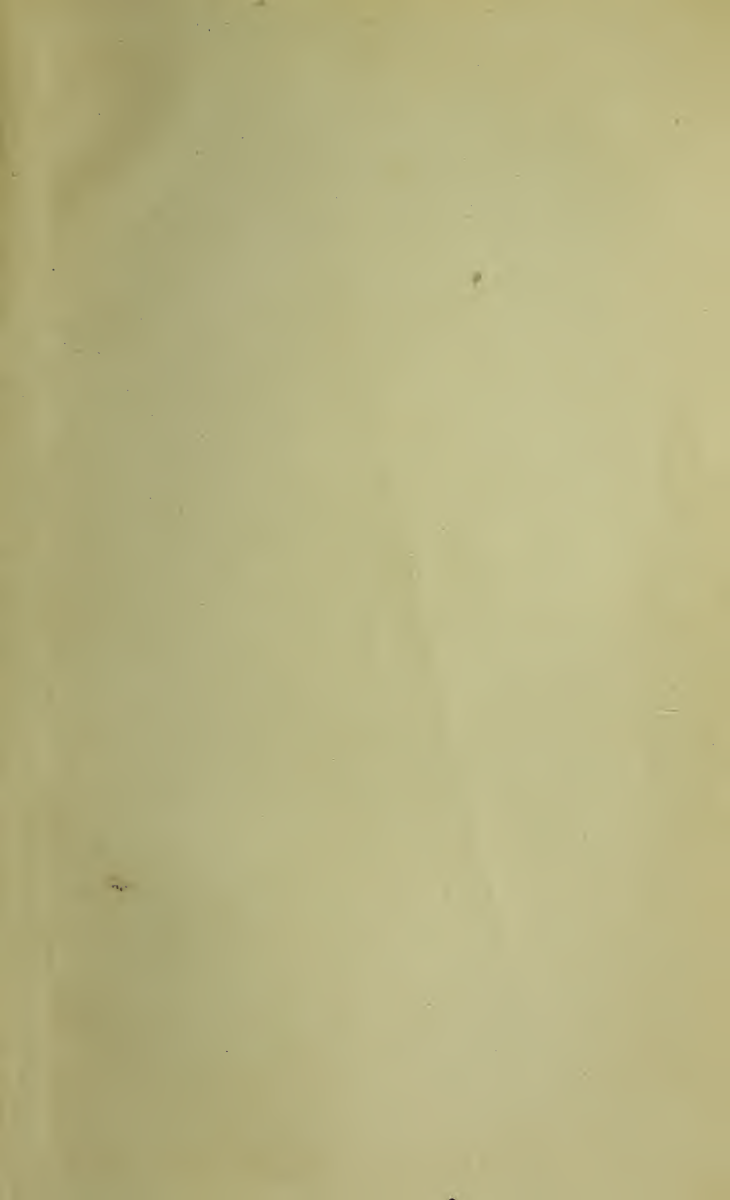
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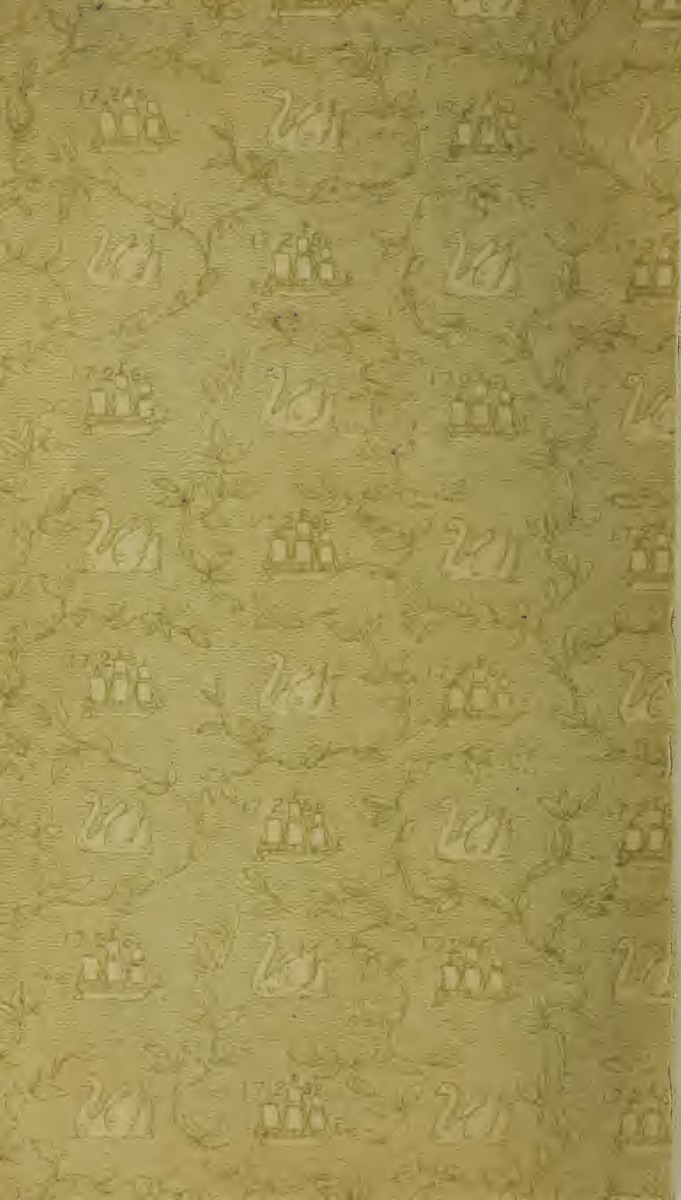
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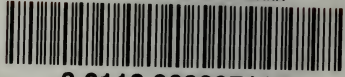
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